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STUDIES ON LIGNIN AND RELATED COMPOUNDS

I. A NEW METHOD FOR THE ISOLATION OF SPRUCE WOOD LIGNIN¹

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Abstract

A description is given of a new method for the isolation from spruce meal of lignin in apparently a relatively unchanged form. The method consists in first extracting the spruce meal with a mixture of equal volumes of benzene and alcohol, followed by an extraction with water. The dried meal is then digested for 6-8 hr. at 110° C. with 8-10 times its weight of ethylene glycol containing 0.2% of iodine, calculated on the weight of spruce meal taken. The reaction mixture is filtered, and the lignin isolated by pouring the filtrate into a large excess of cold water. Other catalysts such as hydrochloric acid may be used in place of iodine and the glycol may be replaced by a variety of hydroxy-compounds such as glycol mono-ethyl ether, glycerol, chlorhydrins, hydroxyacids, etc.

Introduction

The present communication is the first of a series to be published from this laboratory on the chemistry of spruce lignin and related compounds and outlines a method of isolation which it is believed possesses advantages over methods heretofore used, in that the process employed does not subject the wood constituents, during the course of their separation, to experimental conditions of a drastic nature. Subsequent contributions will deal more thoroughly with the structural problem and with the properties of derivatives.

The method developed is not a quantitative one for analytical purposes but serves as a means of isolating, for physical and constitutional studies, the greater portion of those components of wood collectively known as lignin.

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Contribution from the Industrial and Cellulose Chemistry Laboratories, McGill University, Montreal, Canada, with financial assistance from the Canadian Pulp and Paper Association. From a thesis presented by H. J. Rowley in partial fulfilment of the requirements for the degree of Doctor of Philosophy. This work was carried out in 1926-1928 and a preliminary note published in the *Pulp and Paper Magazine of Canada*, International Number, p. 126, 1928.

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A review of the literature (1) dealing with the structure of lignin from various sources appears to indicate a somewhat prevalent belief in the presence therein of a carbonyl group, this, according to certain workers, being present as a conjugated unsaturated aldehyde (5, 7).

In the light of previous investigations carried out on cyclic acetal formation (4) and the assumed aldehydic nature of lignin, there seemed to be a possibility of extracting it from spruce meal by converting the lignin into an acetal, employing for the purpose a polyhydroxy derivative, and a catalyst such as a small quantity of iodine (3) or sulphuric acid (4). This appeared all the more probable in view of the successful use by König (6) of a mixture of glycerol and sulphuric acid for the purification of wood cellulose.

It was found by heating spruce meal (previously extracted with a mixture of alcohol and benzene, followed by water) with about 10 times its weight of ethylene glycol and 0.2% of iodine (calculated on the weight of spruce meal used) at a temperature of 110° C. for about 6-8 hr., that approximately 40% of the wood goes into solution. On filtering the reaction mixture and pouring the solution into a large excess of water, the lignin is precipitated out in the form of a light, buff-colored colloidal product. As indicated in the following communications the glycol appears to be attached to the lignin but the manner of attachment has not yet been definitely settled.

The mode of purification adopted is described in the experimental part.

Other polyhydroxy derivatives such as glycerol, chlorhydrins and hydroxy acids may also be employed in place of glycol. In the meantime Hägglund and co-workers (2) have shown that ethyl, butyl and amyl alcohols can also be used for the same purpose.

Characteristics of Glycol-lignin.

The crude, moist lignin (referred to hereafter as glycol-lignin) is separated by filtration or centrifuging, and is readily soluble in 90% ethyl alcohol and in acetone. It also dissolves readily in dilute (1%) aqueous sodium hydroxide solution at room temperature, but is soluble to only a very slight extent in sodium carbonate.

In the dry state, after purification, it is obtained as a buff-colored powder soluble in 95% alcohol, less soluble in absolute alcohol, and soluble in 60% aqueous acetone at room temperature. It dissolves in 90% acetic acid and in cold dilute 1% alkali, the solubility in alkali decreasing as the alkali concentration increases beyond 5%. It is very difficultly soluble in hot solutions of metallic bisulphites, solution gradually taking place when heated under pressure for about 6-7 days.

The glycol-lignin is free from pentosans (Tollen's method) and may be chlorinated, nitrated, methylated, acetylated, etc.

The yield obtained in the first extraction amounts to 11.15% of the dry weight of the extracted spruce meal and represents 39% of the total lignin present in the original wood.

About 60% of the iodine used as catalyst is converted into hydriodic acid during the course of the reaction. It was found that small amounts of hydrochloric acid can be used in place of iodine as will be indicated in a following communication.

Experimental

White spruce wood*, was reduced to a fine flour with the aid of a disintegrating machine designed in the Forest Products Laboratories, Montreal, and consisting of a large bundle of hack-saws, arranged parallel, face upwards, and clamped together in a horizontal position. These were propelled backwards and forwards against the surface of a small block of the wood held in position in a vertically placed, square, metallic holder by means of a heavy weight. The flour so obtained was classified by screening and that portion passing a 100-mesh sieve was used for extraction.

After drying the wood meal at 60° C. under reduced pressure (20 mm.) it was placed in a cotton bag in an apparatus of the Soxhlet type of sufficient capacity to hold one kilogram of wood meal and extracted for 16 hr. The solvent employed was a mixture of equal volumes of benzene and 95% ethyl alcohol. Excess solvent was then removed by exerting pressure on the cotton bag in the container, followed by a period of air drying, the last traces of solvent being removed at 60° C. under 20 mm. pressure. The wood meal was then extracted with water for 16 hr. and air-dried; the moisture being removed by again heating at 60° C. under 20 mm. pressure.

The meal was then mixed with 10 times its weight of pure ethylene glycol in a three-neck round bottomed pyrex flask, fitted with a motor-driven stirrer and mercury seal, a thermometer and an air condenser.

The flask was immersed in a temperature-controlled oil bath, the contents stirred and brought to a temperature of 110° C. when 2% iodine, based on the dry weight of the wood, was added. The temperature control is important, as it was found that the reaction proceeds much more slowly at 100° C. The mixture was held at 110° C. with vigorous agitation for six hours, the flask removed from the bath and the remaining solids separated from the dissolved portions by filtration on a Büchner funnel. The wood meal residue was thoroughly washed with hot glycol (110° C.) and the filtrate and washings combined.

Treatment of Filtrate

The combined glycol filtrates were then added in a fine stream, from a separatory funnel, to 10 times their volume of distilled water. During the addition the water was rapidly agitated with a mechanical stirrer, and the glycol solution directed into the vortex to ensure thorough and immediate dissemination. A buff-colored, colloidal, flocculent solid at once separated and as soon as stirring ceased began to settle. After three or four hours, about 80% of the supernatant, almost colorless liquor was removed by

*Supplied by the Abitibi Power and Paper Co., Iroquois Falls, Ontario.

siphoning and fresh, distilled water again added, the whole stirred vigorously, allowed to settle, and siphoning resorted to a second time. The procedure of adding fresh water, stirring, and removing the clear liquor was repeated five times; the precaution was always taken to allow the siphon to discharge upon a tared filter paper which was subsequently used in determining the yield. The precipitate was finally collected upon a conical funnel using a tared filter paper. Because of the colloidal nature of the substance, difficulties were encountered in employing a Büchner funnel with suction, although, if just prior to filtration (after the last decantation) the suspension was heated to 70° C. agglomeration occurred and more rapid suction filtration was possible. For purposes of investigation it was found advisable, in most cases, because of the variations in solubility caused by drying, to preserve the material in the moist state. When a dried sample was desired, removal of water was effected by drying over phosphorus pentoxide in a brown glass vacuum desiccator at room temperature. Only in the case of yield determinations was the lignin subjected to higher temperatures. For this purpose a vacuum oven operating at 60° C. was employed.

So long as the lignin remained in contact with water no change in color occurred but removal of water resulted in a darkening of the lignin under the influence of light.

Purification of the Crude Lignin

The moist lignin, containing about 90% moisture, is readily soluble in dilute sodium hydroxide (1%) but since a very small portion is soluble in dilute aqueous sodium carbonate this fraction was removed as follows:

The lignin cake was agitated with sufficient cold 1.0% aqueous sodium hydroxide to dissolve it and then a current of carbon dioxide passed into the solution until a pH value of 8.8 to 8.9 was reached. Glycol-lignin separated out as a flocculent solid, the fraction soluble in sodium carbonate remaining in solution. The mixture was stirred and heated to 50-60° C. to bring about agglomeration. After filtering the glycol-lignin and washing on the filter first with a 0.5% solution of sodium carbonate, then thoroughly with hot water, the cake was re-dissolved in 1.0% sodium hydroxide, re-treated with carbon dioxide, filtered and washed as before. The glycol-lignin was then obtained as a light, buff-colored product by drying over phosphorus pentoxide, under reduced pressure, in the absence of light; it represented 95% by weight of the original crude precipitated lignin.

On acidifying the sodium carbonate solution and washings with phosphoric acid, the small amount of soluble lignin fraction was precipitated as a colloidal substance which, on drying, was much darker in color than the main portion of glycol-lignin.

Treatment of the Residual Wood Meal

After washing the wood meal remaining on the Büchner funnel with hot glycol, it was further washed with hot 95% ethyl alcohol and then transferred to the modified Soxhlet extraction apparatus and further extracted for a period

of six hours with 95% ethyl alcohol to remove completely the glycol- and alcohol-soluble constituents. After a period of air-drying (about 48 hr.), the last traces of alcohol were removed from the meal by heating to 60° C. under reduced pressure; a sample was removed for analysis, and the meal subjected to a second glycol-iodine treatment at 110° C. The separation of the lignin portion was carried out as before, and followed by a similar purification treatment. After a fourth extraction the yield of lignin from the meal became very small.

Treatment of the Alcohol Washings

The alcohol was removed by distillation and the lignin substance held in solution in the residual glycol was recovered by dilution with water in the manner described above. This fraction of lignin, although no difference could be detected by analysis, was not combined with the major portion for purposes of investigation. It was separated and weighed for the purpose of determining the yield.

TABLE I

ANALYSES OF GLYCOL-LIGNIN OBTAINED BY REPEATED EXTRACTION OF SPRUCE MEAL

Glycol-iodine extraction	Description	Yield calculated on original, extracted and dried spruce meal (%)	Percent			
			C	H	O (difference)	OCH ₃
First	Crude glycol-lignin before purification	12.37	64.41	6.08	29.51	18.61
	After purification:					
	(a) Main fraction precipitated by CO ₂		64.65	6.14	29.21	18.79
	(b) Fraction precipitated by H ₃ PO ₄		61.68	5.17	33.15	13.52
Second	Crude glycol-lignin before purification	4.6	64.45	6.16	29.39	18.10
	After purification:					
	(a) Precipitated by CO ₂		64.42	6.19	29.39	17.62
	(b) Precipitated by H ₃ PO ₄		62.78	5.89	31.33	16.11
Third	Crude glycol-lignin before purification					
	After purification:					
	(a) Precipitated by CO ₂		60.54	5.51	33.95	17.41
	(b) Precipitated by H ₃ PO ₄		63.02	5.36	31.62	16.17

NOTE:—Apparently fractions I and II of the purified glycol-lignin, amounting to 17% of the total lignin present in the original spruce meal, are identical in composition, while fraction III is a different product, possibly more closely related to the lignin remaining attached to the cellulose. The nature of the lignin in this residual product is under investigation.

Methylation

Employing 45% potassium hydroxide and dimethyl sulphate and using methyl red as indicator, "methylated lignins" were obtained having methoxyl values of around 26 to 27%. When repeated methylation was resorted to, it was found that the methoxyl content reached a maximum and then fell off slightly to an apparently constant value.

In the case of the lignin, insoluble in sodium carbonate, which was obtained in the first extraction series, and for which data have been given, it was found that the methoxyl content rose from 18.79% to 25.21% with one methylation. A second methylation gave a product having 25.32% methoxyl. A similar lignin product obtained in an extraction series not reported showed upon repeated methylation the changes in methoxyl content given in Table II.

TABLE II
EFFECT OF REPEATED METHYLATION OF GLYCOL-LIGNIN

	% OCH ₃	% C	% H
Before methylation	18.50	64.02	6.19
After first methylation	24.71	—	—
After second methylation	25.75	—	—
After third methylation	27.87	—	—
After fourth methylation	26.12	—	—
After fifth methylation	26.18	65.46	6.19

Nitration

2,165 gm. of twice methylated, purified glycol-lignin, containing 25.9% methoxyl were treated with a mixture of 2.9 cc. of fuming nitric acid and 9 cc. of acetic anhydride at 0° C. for three hours. The methylated glycol-lignin dissolved completely in the nitrating mixture and separated as an orange-red solid on pouring the solution into ice-water. It was filtered and washed, first with water, then with 1% sodium carbonate solution and again with water and dried over phosphorus pentoxide at room temperature for eight days. Yield 130%. Extraction with ethyl ether reduced this value to 116%. Analysis: C, 43.15%; H, 3.45%; N, 10.65%; OCH₃, 14.1%.

The nitrated lignin is readily soluble in ethyl acetate, absolute ethyl alcohol, acetone, methyl alcohol, *n*-butyl alcohol; partly soluble in nitrobenzene; only slightly soluble in glacial acetic acid and in di- and perchlorethylene; insoluble in benzene and petroleum ether (b.p. 35-50° C).*

Chlorination

4.83 gm. of the purified glycol-lignin (Extraction I) was dissolved in ethylene glycol and chlorinated by passing in a current of chlorine at 0° C.

*The properties of nitrated glycol-lignin have been investigated and will form the subject matter of a later communication.

The mixture was poured, with rapid stirring, into 10 times its volume of ice-water and the light golden-yellow precipitate washed thoroughly with water. After drying over phosphorus pentoxide, 6.66 gm. was obtained. Yield 138%.

The material was readily soluble in acetone (60%), and in water; partly soluble in pure acetone. Analysis: C, 45.11%; H, 4.14%; Cl, 20.77%; OCH_3 , 12.22%.

A further investigation of the material is in progress.

Glycol-lignin reacts readily with acyl chlorides in presence of pyridine.

References

1. FUCHS, W. *Die Chemie des Lignins*. 1926.
2. HÄGGLUND, E. and ROSENQUIST, T. *Biochem. Z.* 179:376-383. 1926.
HÄGGLUND, E. and URBAN, H. *Cellulosechemie* 8:69-71. 1927.
3. HIBBERT, H. *J. Am. Chem. Soc.* 37:1748-1763. 1915.
4. HIBBERT, H. and CO-WORKERS. Studies on reactions relating to carbohydrates and polysaccharides. Pts. I-XXV, *J. Am. Chem. Soc.* 1921-1929.
5. KLASON, P. *Ber.* 53:706, 1862, 1864. 1920; 55:448. 1922; 56:300. 1923; 58: 375, 1761. 1925; 61:171, 614. 1928.
6. KÖNIG, F. quoted in Hägglund, E. *Holzchemie*, p. 129, 1928.
7. RASSOW, B. and ZICKMANN. *J. prakt. Chem.* 123: 189. 1929.

STUDIES ON LIGNIN AND RELATED COMPOUNDS

II GLYCOL-LIGNIN AND GLYCOL-ETHER-LIGNIN¹BY HAROLD HIBBERT² AND LÉO MARION³

Abstract

The extraction of spruce wood meal with ethylene glycol in the presence of 0.05% HCl leads to the isolation of a lignin derivative to which the name glycol-lignin is given. If the monomethyl ether of glycol be substituted for the free alcohol, a glycol-ether-lignin is obtained which has a much higher methoxyl content than glycol-lignin. The product of extraction is therefore a compound of lignin and the solvent. A comparison of the methoxyl content of the derivatives obtained from the two lignins by methylation and hydrolysis supports this conclusion. On oxidation, glycol-lignin gives rise to a product which forms a *p*-bromophenylhydrazone, identical with that obtained from the product of the oxidation of ethylene glycol under the same conditions. On hydrolysis with acids glycol-lignin yields, besides 0.7% formaldehyde, a substance which reduces Fehling's solution.

Introduction

Various organic hydroxylic solvents such as glycerol (15), phenol, ethyl, isobutyl and amyl alcohols (6), and thioglycollic acid (13) have been used for the extraction of lignin from wood meal.

In a previous communication (10), it was shown that ethylene glycol is an effective solvent for lignin, when employed in the presence of traces of iodine or dry hydrogen chloride as catalyst. Ethylene glycol, owing to its composition and the impossibility of its undergoing transformations of the type common to glycerol derivatives, is more desirable than the latter as a solvent for lignin; this is particularly true if, as seems to be the case, a compound is actually formed between the solvent and lignin. Phenol has been found to form such a compound when used to dissolve lignin from wood (11, 20); such has also been claimed to be the case with the simple aliphatic alcohols (6), and with thioglycollic acid (13).

The object of the present investigation was to determine the nature of glycol-lignin, isolated by means of ethylene glycol, by a study of the characteristic groups which it contains; also, to ascertain (a) if the material isolated is unchanged lignin, (b) a product of hydrolysis of one of the original components of wood, or (c) a compound formed between lignin and the solvent.

The third possibility (c) has already been considered by investigators working with lignin isolated by various well-known methods, involving the hydrolysis of the cellulosic components of wood. Thus, E. Hägglund and T. Rosenqvist

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(7), who isolated lignin from spruce wood meal by means of ethyl alcohol, considered the product to be an ethoxy acetal. More recently, E. Hägglund and H. Urban (6) succeeded in obtaining an amyl-lignin and a butyl-lignin, each supposedly consisting of a half-acetal derived from one molecule of the corresponding alcohol. The latter, by protecting the aldehyde grouping, was assumed either to prevent polymerization, or to bring about depolymerization, a suggestion first put forward by B. Holmberg and S. Runius (12). The evidence available as to the acetal character of the above derivatives appears inconclusive.

The Extraction of Spruce Wood Meal with Glycol and HCl

Spruce wood meal, previously freed from resins by treatment with a benzene-alcohol mixture, followed by extraction with water, was treated at 100-103° C. with ethylene glycol containing 0.05% of its weight of dry hydrogen chloride. The portion of the wood dissolved amounted to 27% of the original weight. After filtration, the lignin was precipitated from the filtrate by pouring into water; it separated as a greyish-brown colloidal precipitate representing 6% of the total weight of the wood, or 20.4% of the total lignin present in the original spruce meal.

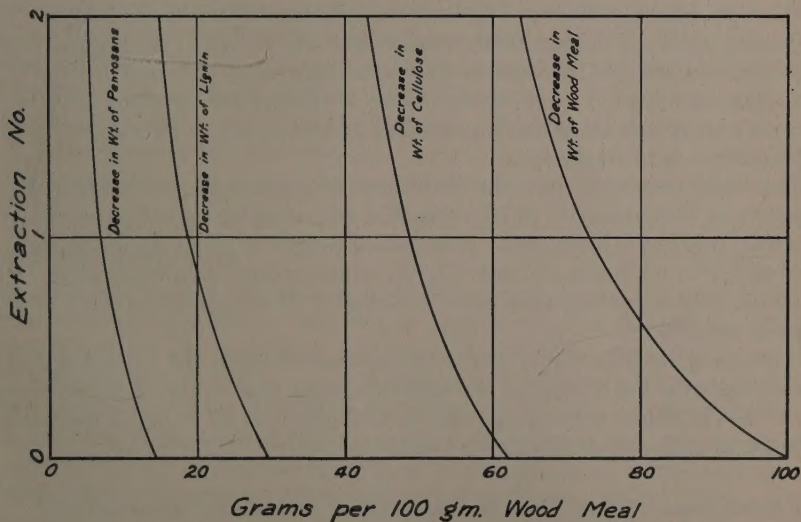


FIG. 1. *Effect of the solvent on the constituents of the wood*

The composition of the residual wood meal, determined after a first and a second extraction respectively (Table II) shows the effect of the extracting medium on the several components of the wood. The figures obtained indicate a gradual decrease in the content of lignin and pentosans, while the cellulose content increases (Table III). If, however, the loss in weight caused by each extraction be taken into consideration in the calculation of the analytical

results, and the latter based entirely on the weight of the wood meal originally taken, the true course of the variation of the components of the wood can be followed more accurately (Table IV). The curves obtained when these results are plotted (Fig. 1) show that the lignin, pentosan, and even cellulose content decrease at the same rate. The fact that the lignin-pentosan ratio remains constant, both in the original wood meal and the residual extracted products, would seem to point to the conclusion that the lignin and pentosans are removed in an integral ratio, thus indicating the probable existence of a chemical combination between cellulose, lignin and pentosans in the original wood.

Glycol-lignin, a greyish, amorphous powder, is soluble in dilute caustic soda, but insoluble in sodium carbonate; hence it contains no carboxyl but one or more hydroxyl groups. It contains no pentosans as determined by the method of Tollens. It was not possible to obtain a molecular weight cryoscopically owing to the abnormal behavior of the substance in organic solvents, anomalous results being obtained in every case. Glycol-lignin had a methoxyl content of 18.5% which was increased to 26.26% by repeated methylation. The methyl groups are not all combined in the same way since hydrolysis of glycol-lignin with 5% sulphuric acid gave rise to a substance with a methoxyl content of 16.42%; hence glycol-lignin contains methyl groups which can be split off by 5% sulphuric acid and others which can not, but are removed by hydriodic acid. The repeatedly methylated glycol-lignin, hydrolysed with 5% sulphuric acid, yielded a substance with a higher methoxyl content (22.37%) than that obtained by hydrolysis of the unmethylated product. At least some of the groups introduced by methylation then are not removed by the 5% sulphuric acid treatment.

The liquor resulting from the hydrolysis of glycol-lignin contains a small quantity of formaldehyde (0.7%) together with a reducing substance which, however, was not investigated. The loss in weight of glycol-lignin on hydrolysis with 5% sulphuric acid was 13.6%, while stronger hydrolysis with 72% sulphuric acid according to Klason's method (17) removed 16-16.5% of the original weight.

If glycol-lignin is in reality a reaction product of lignin and the solvent employed, then the use of another solvent of the same type as glycol, but differing by an easily characterizable group, should give rise to a lignin derivative differing in composition from glycol-lignin by this particular group.

The Extraction of Spruce Wood Meal with Glycol Monomethyl Ether and HCl

If in the extraction of wood, the monomethyl ether of glycol is used in lieu of the free ethylene glycol, the product obtained has a different elementary composition and a higher methoxyl content (20.34%) than glycol-lignin. When hydrolysed with 5% sulphuric acid, however, glycol-ether-lignin gives rise to a product which has the identical methoxyl content (16.45%) found for the hydrolysed glycol-lignin (16.42%). Further, if glycol-ether-lignin is repeatedly methylated, the methoxyl content is raised to 27.45%, which is close to that of exhaustively methylated glycol-lignin; the residue left after

hydrolysis of methylated glycol-ether-lignin with 5% sulphuric acid has also the same methoxyl content (22.12%) as the hydrolysed methylated glycol-lignin (22.37%). The methoxyl values of the various products isolated may be summarized as follows (Table I):

TABLE I
METHOXYL CONTENT OF GLYCOL-LIGNIN AND GLYCOL-ETHER-LIGNIN

Description	% CH ₃ O	
	Glycol-lignin	Glycol-ether-lignin
As isolated	18.50	20.34
After hydrolysis	16.42	16.45
After methylation	26.26	27.45
After methylation and hydrolysis	22.37	22.12

The foregoing experimental facts lead to the conclusion that glycol-lignin is a condensation product of lignin with glycol, and that glycol-ether-lignin is a similar product involving lignin and glycol monomethyl ether, thus accounting for the appreciably higher methoxyl content of the latter compound. The results also suggest that the lignin may be present in the original spruce wood in combination with one or more of the other components (cellulose, the pentosans, hexosans or other carbohydrates), and that the role of the solvent may be the replacement of one or more of these combined components by a glycol or a glycol monomethyl ether radicle. This would be a possible explanation of the similarity in the rates of removal of lignin and cellulose from wood (Fig. 1).

Oxidation of Glycol-lignin

Lignin is very easily decomposed by oxidizing agents; the products, except in the case of alkaline fusion, consisting in general of carbon dioxide, water and some of the lower aliphatic acids. E. Heuser and S. Samuelsen (9) attempted to obtain aromatic derivatives from methylated lignin and methylated lignin-sulphonic acid by alkaline oxidation, but failed. Their claim to have obtained large amounts of oxalic acid is supported by König (16), but questioned by Hägglund (9, p. 67) who obtained acetic but no oxalic acid, in the treatment of lignin either with alkaline permanganate, or with nitric acid.

Glycol-lignin is oxidized completely to soluble products by acid potassium permanganate and from the clear solution, by treatment with *p*-bromphenylhydrazine, a white amorphous derivative is obtained. This product melts at 201°, and contains 14.16% N, 40.38% Br; these figures agree exactly with those required for the di-*p*-bromphenylhydrazone of glyoxal. However, the substance has a Zeisel value of 7.93 and contains 30.82% C and 3.95% H whereas, theoretically, the *p*-bromphenylhydrazone of glyoxal should contain no methoxyl groups and have the composition 42.4% C and 3.03% H.

On the other hand, glycol when oxidized with acid potassium permanganate gives with *p*-bromphenylhydrazine a derivative which on treatment with hydriodic acid by the Zeisel method gives a methoxyl value of 8.02%. The elementary composition of this derivative is in exact agreement with that of the derivative obtained from lignin; the substance melts at 201° C., and when mixed with the latter, retains the same melting point.

The methoxyl value may be explained by the low boiling point of glyoxal (51° C.) and the assumption that the first step of the action of hydriodic acid is to split off the *p*-bromphenylhydrazine, in which case the free aldehyde would be carried over into the absorption tube and reduce the silver nitrate to the metallic state. In fact, the precipitate as weighed was found to be soluble in nitric acid, and therefore to consist of silver. The weight of silver corresponded to the amount which is produced when glyoxal, derived from a quantity of the hydrazone corresponding to the sample taken, is oxidized to glyoxalic acid. Theoretically, the di-*p*-bromphenylhydrazone of glyoxal should contain 42.42% C., and the low carbon content of the compound in hand cannot at the moment be explained. However, since the compound prepared from glycol has not only the same nitrogen and bromine content, but also the identical percentage of carbon, there seems to be no doubt that the two compounds obtained are identical, and are produced from glycol or glyoxal. It is not impossible that the glyoxal may be an oxidation product of the lignin molecule itself, yet the evidence adduced, pointing to the presence of glycol in the molecule, and the known fact that glycol is oxidized by acid permanganate to glyoxal, are strong arguments in favor of the glycol being the precursor of the glyoxal formed.

The oxidation of glycol-lignin with alkaline permanganate did not yield any oxalic acid, but only a trace of a substance smelling strongly of vanillin. Oxidation of fully methylated glycol-lignin gave rise to an acid with the same equivalent as oxalic acid but having different properties.

With the exception of the small quantity of condensation product obtained by interaction with *p*-bromphenylhydrazine, and identified as a derivative of glyoxal, or at all events of a glycol product, permanganate oxidation did not yield any product capable of throwing light on the constitution of lignin.

Experimental

Preparation of Glycol-lignin from Spruce Wood Meal

Spruce wood meal was freed from resins and gums by extraction with a mixture of equal volumes of 95% alcohol and benzene (loss 3.8%), followed by an extraction with water (loss in weight 5.0%), and then dried at 65° C. under 30 mm. pressure for 12 hr. The dried meal was then extracted at 100-103° C. during six hours with 10 times its weight of pure ethylene glycol containing 0.05% hydrogen chloride. The mixture was filtered while hot by means of suction, and the meal washed with about an equal weight of warm glycol followed by the same volume of 95% alcohol.

The alcohol retained by the wood was allowed to evaporate at 50° C. and the residual wood extracted with water in a Soxhlet for 10 hr. This treatment removed the part of the wood rendered soluble by the glycol-HCl extraction. This soluble part consisted chiefly of carbohydrates produced from the pentosans and a fraction of the furfuroids. The residue was dried at 65° C. under 30 mm. pressure. The total loss in weight of the original wood meal in the first extraction with glycol-HCl and the subsequent water extraction amounted to about 27%.

A second extraction of the thoroughly dried residue with ethylene glycol under the same conditions, removed a further 15%, or 9.5% calculated on the weight of meal originally taken. The loss in weight of the wood after each extraction in a typical case, together with the analysis of the residual meal are given in Table II.

TABLE II
EXTRACTION OF WOOD MEAL WITH GLYCOL—HCl

Description	Dry weight, in gm.	Loss in weight, in gm.	% Loss on original wood meal	Weight of lignin isolated, in gm.	Lignin extracted, per cent of total lignin
Original wood meal (extracted with alc.-benz. and water)	468.1	—	—	—	—
1st Extraction (glycol - HCl and water)	341.3	126.8	27.1	28.2	20.5
2nd Extraction (glycol - HCl and water)	297.0	44.3	9.5	11.3	8.2

TABLE III
ANALYSIS OF WOOD MEAL AFTER EACH EXTRACTION

Sample of wood meal residue	Lignin ¹ per cent	Pentosans ² per cent	Cellulose ³ per cent
Original meal extracted with alcohol-benzene and water	29.40	14.30	61.85
After 1st extraction with glycol-HCl and water	25.45	9.46	66.82
After 2nd extraction with glycol-HCl and water	23.40	8.18	67.80
After 3rd extraction with glycol-HCl and water	23.03	7.18	68.36

1. Lignin was determined according to Klason's method (19).

2. Pentosans were determined by the method of Tollens (8).

3. The cellulose content was determined by the method of Ross, Davidson and Houghton (18).

The figures of Table III have been recalculated on the basis of 100 gm. as the weight of original wood meal in order to take into account the loss in weight caused by each extraction. These values are given in Table IV, and represented graphically in Fig. 1.

TABLE IV
ANALYTICAL FIGURES BASED ON WEIGHT OF ORIGINAL WOOD MEAL*

Sample of wood meal residue	Relative weights after extraction	% Lignin calculated on wt. of original meal	% Pentosans calculated on wt. of original meal	% Cellulose calculated on wt. of original meal
Original wood meal extracted with alcohol-benzene and with water	100	29.40	14.30	61.85
After 1st extraction with glycol-HCl and with water	72.8	18.59	6.89	48.7
After 2nd extraction with glycol-HCl and water	63.4	14.84	5.18	43.0

*These weights, calculated on a 100-gram basis, are obtained from the dry weights given in Table II.

Treatment of Glycol Solution

The glycol-lignin is recovered from the reddish-brown glycol extract by slowly pouring the latter, in a fine stream, into 10 times its volume of cold water kept well stirred. Glycol-lignin separates as a flocculent precipitate which settles slowly on standing. After washing by decantation several times and filtering, it is stirred into a 10% solution of sodium carbonate which dissolves about 0.05-0.1%. The residue is then filtered, washed and dissolved in dilute sodium hydroxide (1%). The solution is acidified with dilute sulphuric acid, and the precipitated lignin washed, filtered with suction, washed again, and dissolved in 95% alcohol. After passage through a filter to remove a small insoluble residue, the alcoholic solution is boiled under reflux for 20 min. with a small amount of freshly prepared zinc-copper couple, and filtered. The glycol-lignin is obtained as a light-colored product by pouring the clear filtrate into water containing a trace of acetic acid to help coagulation. The product, when filtered, washed and dried in a vacuum desiccator over phosphoric pentoxide, is a greyish amorphous powder which darkens when heated to 176° C., but undergoes no further visible change even at 250° C. It is soluble in warm glycol, 90% alcohol, phenol, dimethyl propylene glycol, aqueous acetone, methyl cyanide, warm acetophenone, monochloroacetic acid; very slightly soluble in glacial acetic acid, camphor and pyridine; insoluble in benzene, ether, water, chloroform, etc. Analysis:—Found: C, 60.83, 61.42, 61.51%; H, 6.13, 6.13, 6.17%; CH₃O, 18.56, 18.24, 18.50%; CH₃CO, (as HAc) 3.75%.

Hydrolysis of Glycol-lignin

The method used was that of E. Fischer (3a, p. 923): Glycol-lignin (5.00 gm.), suspended in 100 cc. 5% sulphuric acid was heated in a steam bath under reflux condenser for 100 hr.; the mixture was then allowed to cool, and was filtered. The residue was washed thoroughly, dried and weighed (4.32 gm.). Loss 13.6%. The filtrate (A) was retained for further investigation. The hydrolyzed product was a brown amorphous powder, insoluble in sodium hydroxide

and sodium carbonate and in all organic solvents tried. Analysis:— Found: C, 63.33, 63.22%; H, 5.77, 5.74%; CH_3O , 16.60, 16.21, 16.42%. On the other hand, hydrolysis of glycol-lignin with 72% sulphuric acid, according to Klason's method (17) removed a greater percentage weight. The losses recorded on different samples were 16.0, 16.5, 15.5, 16.8%.

Analysis of Hydrolysis Liquor (A)

(a) Formaldehyde

Formaldehyde was detected qualitatively in the filtrate from the hydrolysis of the glycol-lignin by the standard phenol-sulphuric acid test and the ferric chloride-sulphuric acid test. Furfuraldehyde does not respond to either of these tests.

Formaldehyde was determined quantitatively by the method employed by Freudenberg and Harder (4). Glycol-lignin (2.6909 gm.) was distilled with HCl exactly as in the determination of pentosans by Tollens' method and the distillate (360 cc.) extracted with ether in a continuous extraction apparatus for 12 hr. After separation from the ether extract, the aqueous distillate was poured into 100 cc. of a concentrated solution of barbituric acid in 12% hydrochloric acid, and allowed to stand in the ice chest for four days. After the second day a fine crystalline, bright yellow precipitate of the condensation product of formaldehyde with barbituric acid ($\text{C}_9\text{H}_8\text{O}_6\text{N}_4$) began to separate. The precipitate was filtered through a microfilter, washed with 50 cc. water, dried at 100°C . and weighed. Weight of product 0.1691 gm., formaldehyde 0.0189 gm., or 0.7%. The accuracy of the method was tested by its application to a solution of known formaldehyde content: 10 cc. of the solution gave 0.2839 gm. condensation product corresponding to 0.0318 gm. formaldehyde. Two 10 cc. portions from the same solution analyzed by Romijn's iodometric method (1) gave: 0.0333, and 0.0332 gm. $\text{H}\cdot\text{CHO}$. These results show that, using the barbituric acid method, an indicated content of about 95% of the formaldehyde present, as determined by the standard iodometric analysis, is obtained.

(b) Reducing Value of the Hydrolysis Liquor. (A)

The hydrolysis liquor (A) was found to reduce Fehling's solution and a quantitative estimation of this property was carried out by means of Bertrand's method (2). The liquor was neutralized with barium carbonate, filtered and sulphuric acid added to the filtrate (110 cc.) to give a concentration of 1%. It was then evaporated to about 75 cc. and the volume brought to exactly 100 cc. with water. 30 cc. was then treated according to the procedure given by Bertrand and the weight of cuprous oxide determined calculated to mg. of copper. The liquor produced from the hydrolysis of 3.0357 gm. glycol-lignin possessed a reducing power equivalent to 73 mg. copper or 24 mg. copper per gm. of lignin. Formaldehyde, produced in the course of hydrolysis, is all driven off in the process of evaporation of the filtrate prior to the application of Bertrand's method; the reducing power of the solution must then be due to some other factor.

Treatment of the hydrolysis liquor with *p*-nitrophenylhydrazine yielded but a small amount of an amorphous substance which did not melt below 261° C. (N, 17.64%; CH₃O, nil). All attempts to identify glycol in this liquor failed.

Methylation of Glycol-lignin.

Glycol-lignin (1.1 gm.) was dissolved in 1% aqueous potassium hydroxide and methylated by means of 50 cc. of 45% potassium hydroxide and 50 cc. dimethyl sulphate, each reagent being added gradually at such a rate as to maintain the mixture as nearly neutral as possible. Gradually the product was thrown out of solution, and after one hour the mixture was acidified and filtered. The operation was repeated twice, each time with 25 cc. each of 45% potassium hydroxide and dimethyl sulphate, the methoxyl content not being increased by further treatment. Yield 1.0 gm. The methylated product was dissolved in alcohol, the solution refluxed with a small amount of freshly prepared zinc-copper couple, to remove the color, filtered and poured into water. The precipitated, methylated glycol-lignin, filtered and dried, is a greyish, amorphous powder, soluble in alcohol and acetone but insoluble in ether, chloroform and benzene. It is also insoluble in sodium hydroxide and sodium carbonate. Analysis:— Found: C, 63.87, 63.52%; H, 6.42, 6.35%; CH₃O, 26.77, 26.70, 26.30%.

Hydrolysis of Methylated Glycol-lignin

Completely methylated glycol-lignin loses 25.8% of its weight when hydrolyzed with 5% sulphuric acid under the same conditions used for the hydrolysis of glycol-lignin. The residual product, a brown powder, is insoluble in alkalis and in organic solvents. Analysis:— CH₃O, 22.83, 22.37%.

Extraction of Wood Meal with Ethylene Glycol Monomethyl Ether.

The procedure used was the same as that employed in the extraction of wood meal with ethylene glycol except that 0.1% instead of 0.05% of dry hydrogen chloride was used. The product, purified exactly as in the case of glycol-lignin and dried over phosphoric anhydride in vacuo was a light brown amorphous substance, soluble in sodium hydroxide, alcohol, chloroform, glycol monomethyl ether; insoluble in benzene, ether and sodium carbonate. Analysis:— C, 64.36, 64.39%; H, 6.45, 6.53%; CH₃O, 21.45, 21.39%.

Hydrolysis of Glycol-ether-lignin

The hydrolysis was carried out as in the case of glycol-lignin using 5% sulphuric acid at 100° C. The residue (87.7% of the original) was a brown, amorphous powder, insoluble in alkalis as well as in all the usual organic solvents. Analysis:— CH₃O, 16.62, 16.45%.

Methylation of Glycol-ether-lignin

Glycol-ether-lignin, dissolved in 1% potassium hydroxide was methylated with dimethyl sulphate and 45% potassium hydroxide, as in the case of glycol-lignin, and purified in the same way from alcoholic solution. The product, dried over phosphoric anhydride in vacuo, is a very light brown, amorphous

powder, soluble in moist acetone and alcohol, but insoluble in benzene, chloroform and ether. Analysis:— C, 64.62, 64.42%; H, 6.93, 6.49%; CH_3O , 27.45, 27.45%.

On hydrolysis under the same conditions as in the other cases, this methylated product lost 34.2% of its weight. The residue was a brown amorphous powder, insoluble in alkalis and organic solvents. Analysis:— CH_3O , 22.12, 22.13%.

Oxidation of Glycol-lignin

In alkaline solution

Glycol-lignin when oxidized with alkaline potassium permanganate did not yield any oxalic acid. On the other hand, oxidation of methylated glycol-lignin in acetone solution gave rise to an acid product. 2.10 gm. methylated glycol-lignin was dissolved in 100 cc. acetone purified by previous treatment with alkaline potassium permanganate, and mixed with a solution of 0.6 gm. potassium permanganate in 20 cc. acetone, the mixture being allowed to stand two days at room temperature. It was then stirred for eight hours and the manganese dioxide sludge allowed to settle. Several more additions of potassium permanganate, dissolved in acetone, were then made, the solution being stirred for eight hours after each addition. After a total addition of 2.1 gm. potassium permanganate, oxidation was complete as indicated by the permanence of the light purple color. The excess of permanganate was destroyed with sulphurous acid, the acetone removed by distillation under reduced pressure, and the volume of the residual solution made up to 100 cc. exactly. This was divided into different portions and treated as follows: (a) Two 10 cc. portions, titrated against 0.1080 N alkali, required 4.38, and 4.39 cc.; hence the total solution (100 cc.) was equivalent to 0.1894 gm. NaOH. The sulphuric acid present, determined as barium sulphate, was equivalent to 0.0151 gm. NaOH so that the solution contained the equivalent of 0.1743 gm. in organic acid or acids.

(b) Two 10 cc. portions were each diluted with 50 cc. water, acidified with 15 cc. of 1:1 sulphuric acid, heated to boiling, and titrated against 0.1156 N potassium permanganate; KMnO_4 used was 4.90 cc. and 4.79 cc. respectively. For the total solution, this is equivalent to 48.5 cc. of potassium permanganate, which is more than oxalic acid would require.

(c) A further portion of the solution when tested for oxalic acid by means of calcium chloride gave a negative result.

Oxidation in acid solution

Oxidation with a solution of chromic acid in glacial acetic acid did not yield any results of value, but the use of acid potassium permanganate proved of interest.

35 cc. of 5% potassium permanganate, mixed with 100 cc. of 1:1 sulphuric acid, was added to a suspension of 1 gm. glycol-lignin in water kept in agitation by a stream of air which was filtered through a wad of cotton. Fresh additions of the same quantities of acid and potassium permanganate solution were made until the glycol-lignin suspension disappeared and the liquid became colorless. To this clear solution was then added 0.5 gm. *p*-bromphenylhydrazine dissolved in a mixture of 6 cc. warm water and 2 cc. 50% acetic acid. A white precipitate separated on standing; it was filtered, washed with dilute acetic acid, then with water, and dried in a vacuum over phosphoric anhydride. The product separated from alcoholic solution on dilution as a white amorphous substance, having a pinkish shade. It was soluble in warm glacial acetic acid, dilute alcohol and pyridine; insoluble in ligroin, ethyl acetate and benzene, and decomposed on warming with ethylene bromide. It turned red on heating to 195° and melted at 201° C. with decomposition. Analysis:— Found: C, 30.75, 30.73, 30.82%; H, 3.95, 4.51, 4.39%; N, 13.72, 14.16%; Br, 40.38%; CH₃O, 7.93, 7.45, 7.62%. Required for C₁₄H₁₂N₄Br₂: N, 14.14% Br, 40.4%.

An attempt was made to prepare the di-*p*-bromphenylhydrazone of glyoxal. Glyoxal was prepared from glycol by oxidation with potassium permanganate and sulphuric acid (3). To 10 drops of ethylene glycol, 10 cc. water and 0.5 cc. concentrated sulphuric acid were added, and the mixture heated to boiling. The glycol in the solution was oxidized by the addition of 0.5 cc. of 2% potassium permanganate, and the clear solution allowed to stand for one minute. This solution was mixed with a filtered solution of 0.5 gm. *p*-bromphenylhydrazine dissolved in 6 cc. warm water and 1.7 cc. 50% acetic acid, a white precipitate forming almost immediately. The product was filtered, washed with water, then with alcohol and with ether, and dried over phosphoric anhydride. The white powder so obtained turned brown at 190° C. and melted at 200° C. with decomposition.

Analysis:— C, 30.81%; H, 4.57%. 3.114 mg. gave 1.891 mg. AgI equivalent to 8.02% CH₃O. A mixture of glyoxal *p*-bromphenylhydrazone with the *p*-bromphenylhydrazine derivative of the oxidation product of glycol-lignin melted with decomposition at 201°. The two products therefore appeared to be identical.

References

1. ALLEN's Organic Analysis, Philadelphia, 1924, p. 329.
2. BERTRAND, G. Bull. Soc. Chim. (3) 35:1285-1299. 1906.
3. DENIGÈS, G. Ann. Chim. (8) 18:175. 1909.
- 3a. FISCHER, E. and FREUDENBERG, K. Ber. 45:915-935. 1912.
4. FREUDENBERG, K. and HARDER, M. Ber. 60:581-585. 1927.
5. FRIEDRICH, A. Z. physiol. chem. 176:127-143. 1928.
6. HÄGGLUND, E. and URBAN, H. Cellulosechemie. 8:69-71. 1927; 9:49-53. 1928.
7. HÄGGLUND, E. and ROSENQVIST, T. Biochem. Z. 179:376-383. 1926.
8. HAWLEY, L. F. and WISE, L. E. The Chemistry of Wood, New York, 1926.

9. HEUSER, E. and SAMUELSEN, S. *Cellulosechemie*. 3:78-83. 1922.
10. HIBBERT, H. and ROWLEY, H. J. *Can. J. Research*, 2: 357-363. 1930.
11. HILLMER, A. *Cellulosechemie*. 6:169-187. 1925.
12. HOLMBERG, B. and RUNIUS, S. *Svensk Kemisk Tidskrift*, 37:189. 1925.
13. HOLMBERG, B. *Papier-Fabr.* 26:556. 1928.
14. JONAS, K. G. *Z. angew. Chem.* 34:289-291. 1921.
15. KÖNIG, J. *Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe*. 1911, p. 292.
16. KÖNIG, J. *Cellulosechemie*. 2:105-113. 1921.
17. LAGELER, E. *Cellulosechemie*. 4:61-62. 1923.
18. ROSS, J. H., DAVIDSON, A. L. and HAUGHTON, E. O. *Pulp Paper Mag. Can.* 27:925-926. 1929.
19. SCHORGER, A. W. *The Chemistry of Cellulose and Wood*, New York, 1928, p. 163.
20. WEDEKIND, E. and KATZ, J. R. *Ber.* 62:1172-1177. 1929.

ON THE HYDROGENATION OF BITUMEN FROM THE BITUMINOUS SANDS OF ALBERTA¹

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Abstract

Bitumen from Alberta bituminous sands, hydrogenated at high temperatures and pressures, has been found to form a light crude oil, amounting under favorable conditions to 80% or more of the original bitumen. It is believed that this yield can be increased by the use of a more efficient apparatus. The optimum temperature was in the region of 380° C., and the best catalysts used were ammonium molybdate and aluminum chloride. An absorption of hydrogen equivalent to 3% by weight of bitumen was easily attained. The oil had a sulphur content equal to about one-half that of the bitumen; it is easily refined to produce a stable, white gasoline.

Introduction

The Province of Alberta possesses in its resources (1, 3, 9) of coal, bituminous sands and natural gas, three of the world's larger supplies of hydrocarbons. None of these resources are utilized to any great extent, and further, a tremendous wastage occurs in the case of natural gas. The product of those gas wells which are "wet" is treated to remove the naphtha. The resulting dry gas, largely methane, is utilized only in part, and the greater portion is destroyed by burning in the field. Apart from this direct loss, largely confined to the Turner Valley, there are many other dry gas wells at present capped. In 1926, the possible daily production in excess of requirements was some 400 million cu. ft. (2), of which approximately 40 million cu. ft. was destroyed in the Turner Valley. The increased production in the Valley since 1926 has led to an excess production and direct loss of four to five times the above figure. Moreover, production is increasing at a greater rate than the demand. A number of methods of conserving or utilizing this waste gas have been suggested from time to time without, however, any practical development.

An interesting and promising field for natural gas lies in its use as a raw material in chemical industry, either directly or as a source of gases more amenable to chemical change. For some years a variety of experiments on these lines have been carried on and this paper gives a preliminary account of one of the projects undertaken.

The use of natural gas as a source of hydrogen has been shown to offer no difficulties. From the industrial point of view, the processes of hydrogenation of tar, coal or oils are largely dependent for success on an adequate and cheap supply of hydrogen. The present paper deals with one part of this work only; the hydrogenation of coal and the possibility of using natural gas directly as a hydrogenating agent are reserved for a subsequent communication.

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Materials

Bitumen was obtained through the kindness of Dr. K. A. Clark and was prepared from McMurray sands by his separation process (4). Briefly, in this process, the sand is intimately mixed with sodium silicate solution, heated, and added to a large volume of hot salt water. The bitumen separates and collects on the surface of the water. The general characteristics of the crude bitumen may be seen from the following analysis:

Sulphur.....	4.16%
Water.....	1.0%
Carbon residue.....	14.3%
Density (25° C.).....	0.9984

It may be of interest to point out that the sulphur content is lower than that usually found (7). The common method of assaying bituminous sand is by extraction with a solvent, such as carbon disulphide or benzene, followed by distillation to remove the solvent. Sulphur determinations on bitumen, extracted by sulphur-free benzene from the same sand as used by Dr. Clark, gave 4.66% (hot extraction) and 4.50% (cold extraction). It is evident that the method of separation influences to some extent the sulphur content of the bitumen.

Before use, the bitumen was dehydrated by heat at 110-120° C., which process involved very little loss of material. Commercial electrolytic hydrogen, stored in steel cylinders, was used directly in this work. Different catalytic materials, all ground to pass 100 mesh, were used. For convenience in tabulation they are labeled A to F and have the following composition:

- A, ammonium molybdate,
- B, ammonium molybdate and iron oxide in equal parts,
- C, anhydrous aluminum chloride,
- D, alkalized iron oxide,
- E, iron, chromium and nickel oxides in equal parts,
- F, nickel oxide.

No attempt was made to prevent any catalytic effect that the steel autoclave might have on the reactants.

Apparatus

Essentially the apparatus consisted of a compressor and gas storage system for operation under pressures up to 5,000 lb. per sq. in., and an alloy steel autoclave designed and tested to stand 7,500 lb. at 500° C. Operating conditions have varied from 200 to 450° C. at pressures up to 5,000 lb. The autoclave showed few signs of deterioration and where care was exerted, was absolutely gas-tight under the above operating conditions.

The flanged autoclave body was machined from solid stock to three inches inside diameter; when fully equipped for operation it had a capacity of 850 cc. The cover was bolted on by eight stout studs, a tight joint being obtained by the pressure of a tongue in the cover on an annealed copper ring placed in an annular groove in the autoclave body. Inlet and outlet valves were provided on the cover which also carried a thermometer pocket, and an anchor type stirrer with its water-cooled gland and necessary gearing, which was operated at 40 r.p.m. The autoclave was supported vertically in an electric furnace. It may be pointed out here that this autoclave is not the best for the purpose in hand for a variety of reasons, chief of which is a lack of uniform temperature and poor agitation. A new and much larger autoclave has been constructed for the continuation of this work.*

Temperatures were measured by mercury thermometers or by iron-constantan thermocouples connected to a Leeds and Northrup recording controller. They are correct to 3° C. Pressures in pounds per square inch were measured on Bourdon tube gauges, calibrated by comparison with a standard test gauge reading to 25 lb. per sq. in.

Procedure

A sufficient quantity of the catalyst was incorporated with bitumen to give the desired ratio, and a weighed amount, usually between 300 and 400 gm. was placed in the clean autoclave. The autoclave was closed, the connections made, and the air washed out, the pressure being then raised with hydrogen to the initial value. The temperature was raised as rapidly as possible and held to the desired value by hand regulation until steady, when the controller was cut in. Pressures were recorded continuously, or otherwise read and noted at appropriate intervals. Stirring was commenced when the temperature was such that the charge was fluid. Two subsequent procedures were followed. In some instances, after the reaction was complete, the autoclave was cooled and the gas liberated into a gas holder through a test meter. The gas was analyzed after it had reached uniform composition in the gas holder. A further addition of hydrogen could then be made and the process repeated a number of times, or alternatively, the autoclave might be opened after one addition. In other experiments, after absorption appeared complete, more hydrogen was added as often as wanted without allowing the autoclave to cool or removing the residual gas. Finally the autoclave was cooled and the gas measured and collected for analysis. A considerable quantity of the more volatile hydrocarbons passed over with the gas and were collected in a condenser immersed in solid carbon dioxide. They boiled over the range -40 to +40° C. and were doubtless largely butane and pentane with some propane. They amounted to 2 to 3% of the original bitumen.

**Preliminary experiments on bitumen, in a larger autoclave having uniform temperature distribution and efficient agitation, showed very rapid hydrogen absorption commencing at 350° C. At 380° C., the pressure dropped at 600 lb. per hour, and no coke was produced. At 400° C., the pressure drop was 800 lb. per hour and 2-3% of coke was produced.*

The oil and coke were separated and weighed. No treatment was used to remove adhering oil from the coke other than allowing the excess oil to drain thoroughly. When possible, the oil was examined for density, viscosity, carbon residue, solubility in sulphuric acid, distillation range and sulphur content. Ultimate analyses and some refining tests have been carried out but are incomplete at present. Densities were determined at 25° C. with a 10 cc. density bottle. Viscosities were found when possible with an Ostwald pipette and are recorded as poises at 25° C. Unsaturation was determined by solubility in sulphuric acid according to the method of the United States Bureau of Mines with centrifugal separation. Carbon residue was determined with Conradson's apparatus and the distillation range was found by the A.S.T.M. kerosene distillation apparatus.

For a number of reasons, sulphur was not determined by any of the common methods. Accuracy and, because of the large number of determinations, speed, were desired. The lamp method was useless on the oils produced from bitumen because of suspended colloidal carbon and mineral matter. The oxygen bomb is accurate but tedious and time consuming. The Escha and sodium peroxide methods are inaccurate unless a great deal of time and care are taken. Other work on the determination of total sulphur in gases led to a satisfactory method. Weighed oil samples, held in sulphur-free siliceous earth, were placed in a quartz tube heated electrically as customary in organic combustion analysis. The tube was packed with platinum and kept at 900° C., except in the region of the oil sample. Provision was made to raise the temperature of the oil slowly to 900° C. and at the same time to have a brisk stream of air passing through the tube. The oil was volatilized and burnt completely; the products of combustion in the air stream were washed by standard sodium carbonate solution and the quantity of sulphur dioxide determined by titration with standard hydrochloric acid. The method was tested with pure sulphanilic acid and found satisfactory even in the presence of so much combined nitrogen. Blank test runs showed that no correction was necessary. A determination requires 1.5 to 2 hr. and the method is applicable to solids or liquids even as volatile as benzene. Duplicates agree to better than 0.01%, using one-gram samples of oil containing 2% sulphur. If such accuracy is not desired, considerable time can be saved by increasing the air flow and using smaller samples.

Results and Discussion

The chief experimental details of representative experiments are given in Tables I and II. As is evident, there is a considerable discrepancy in many cases in material balance. This loss may be due to several causes: first, leaks in the autoclave joint at high temperatures; second, loss of volatile constituents in the gas as vapors and in some cases as foam; and lastly, loss of oil by evaporation after opening the autoclave. A small amount of coke was lost due to the difficulty experienced in its removal from the autoclave walls but it is probable

that nearly the same amount was left in the autoclave from the preceding experiment. It is to be noted that the sources of loss would all lead to a decrease in the yield of oil. In experiments 34 and 40, obvious leaks occurred and no calculation of gas yield or hydrogen absorption could be made.

TABLE I
DETAILS AND RESULTS OF HYDROGENATION OF BITUMEN

Experiment No.	23	25	26	29	30	31	34	36	37	38	39	40	47
Catalyst %	none	none	1.4A	1.3A	2.7B	1.4A	0.4A	0.5A	1.6C	none	0.6D	0.6E	0.6F
Maximum temperature, deg. C.	375	410	380	380	400	385	407	418	435	400	410	407	418
Average temperature, deg. C.	340	380	360	360	380	380	400	400	400	400	400	400	400
Initial pressure, lb. per sq. in.	710	1175	1175	1175	1175	1175	1175	1165	1080	1220	1160	1360	1200
Maximum pressure, lb. per sq. in.	1175	2470	1865	1830	2930	3370	3360	3090	2360	2970	2690	2500	2400
Additions	1	none	3	3	5	6	6	2	5	2	1	1	1
Final pressure, lb. per sq. in.	615	825	490	565	835	935	575	1015	995	900	845	600	800
Time, hr.	6	5	8	18	30	8	24	11	30	9	9	12	8
Bitumen as oil, %	89.6	73.8	73.4	92.8	85.9	68.0	69.6	55.0	71.5	74.5	72.5	64.3	73.5
Bitumen as coke, %	0.0	23.6	21.1	0.0	10.0	18.0	3.6	42.4	11.4	10.5	19.1	14.3	17.1
Gas, less H ₂ , litres per kg. bitumen	8.5	66.0	26.3	33.0	53.7	120	—	180	133	69.3	85.0	—	96.5
Bitumen gasified, %	0.6	—	—	2.8	5.6	9.3	—	17.5	9.0	5.6	6.5	—	5.7
Loss, %	9.8	2.6	5.5	4.3	0.0	4.7	19.5	0.0	8.1	9.4	1.9	18.9	3.7
Hydrogen absorbed, %	0.37	0.67	1.2	1.0	2.2	3.0	—	1.9	2.8	1.5	1.2	—	1.3

The character of the crude oils is indicated by the data of Table II. They are black or dark brown in color because of suspended carbon, but lose much of this carbon on settling. The distillate is straw-yellow and deposits gums with a lightening of color on standing for a few days. The sulphur content is about half that of the original bitumen and much of the remainder appears as hydrogen sulphide in the gas. The unsaturation value is high but does not indicate the true unsaturated compounds so much as those hydrocarbons and tar acids soluble in sulphuric acid. Preliminary refining experiments involved a sulphuric acid wash in the ratio of one part acid to thirty parts oil, an alkali wash and distillation. The washing process produced a straw-yellow oil of good odor having a water-white gasoline distillate that did not deteriorate on standing. The residue showed a slight darkening in color but no decomposition to carbon. Quantitative data are lacking in such small scale experiments but the quantity of sludge from the washing process did not appear excessive.

The rate of hydrogen absorption is most important and is readily indicated by the variation of pressure with time. In Fig. I are plotted the results of Experiments 25, 26 and 38. In the cases of 26 and 38 respectively, three and

TABLE II
PROPERTIES OF OILS

Experiment No.	23	25	26	29	30	31	34	36	37	38	39	40	47
Density at 25°C.	.993	.920	.926	.969	.914	.874	.890	.852	.878	.887	.891	.915	.898
Viscosity at 25° C.	—	.052	.160	—	.033	.025	.022	.012	.026	.033	.030	.042	.029
Carbon residue, %	14.1	7.5	6.7	11.3	5.6	3.4	4.4	2.5	4.3	5.6	6.4	8.5	6.2
Unsaturation, %	—	49	48	—	45	20	23	34	32	39	38	64	52
Sulphur, %	—	2.46	—	—	2.24	—	—	—	1.40	2.36	2.60	—	2.09
Initial B.P., deg. C.	105	48	60	110	60	42	38	36	35	40	37	45	43
Vol. % at 200°C.	9	38	22	8	30	45	40	45	40	33	38	34	35
Vol. % at 300°C.	47	62	45	28	58	70	65	70	68	60	62	62	65
End-point	319	341	348	319	331	355	363	359	354	353	338	341	325
Pitch, %	32	18	20	30	24	16	20	22	20	20	26	25	27
M.P. pitch	—	—	—	130	55	53	80	—	52	75	37	71	—

one successive additions of hydrogen were made. The effect of temperature and of a catalyst are made evident in these curves. No catalyst was used in Experiments 25 and 38 and the temperatures were 380 and 400° C. The rate of absorption is much greater at the higher temperature. The effect of the catalyst is shown in Experiment 26 at a temperature of 360° C. In spite of the lower temperature the rate of absorption, as shown by the slope of the curve, is greater. The effect of temperature is very important and makes it difficult to follow the reaction by pressure readings. Below 360° C., the reaction is very slow and about equal to the rate at which gaseous hydrocarbons are produced by cracking. The pressure remains practically constant even though hydrogen is being absorbed, as shown by subsequent analysis. At 400° C., absorption is rapid but at the same time cracking is rapid, and the pressure remains constant. In many instances an initial drop in pressure occurred at 400° C. which was followed shortly by a steady increase due to the production of methane and like hydrocarbons. The last half of Experiment 38 is typical of this behavior. Experiment 39, however, demonstrates the other

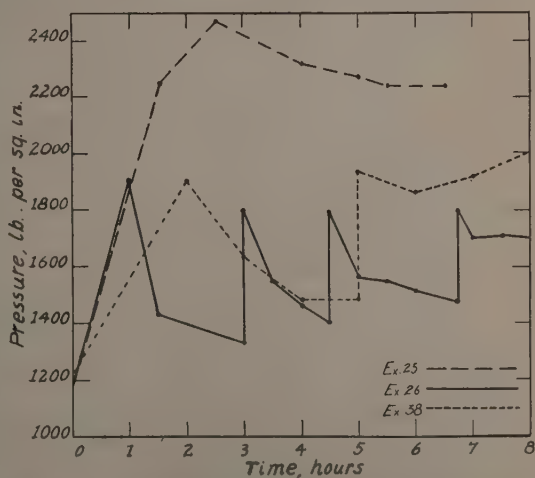


FIG. 1. Time-pressure chart in the hydrogenation of bitumen.

case. The pressure reached a constant maximum value of 1,890 lb. and the hydrogen concentration dropped to 45%. A further addition of hydrogen produced a constant pressure of 2,600 lb. and a final hydrogen concentration of 48%.

Fig. 1 indicates clearly that absorption apparently ceases when the pressure has dropped to two-thirds the maximum value; the partial pressure of hydrogen being much less, in general one-fifth to one-sixth of the maximum pressure or one-half of the final cold pressure. These figures are subject to wide variation in individual cases but are representative. In the absence of a catalyst, the pressure of hydrogen when absorption ceases is usually higher.

From the practical point of view, the time is important. The curves show that the bulk of the reaction occurs in the first two hours and most of that in one hour. Because of the steady production of gaseous hydrocarbons these figures are to be considered only as minimum values. Generally, three to four hours were allowed for absorption. In production of quantities of oil, the hydrogen pressure would necessarily be maintained at the maximum pressures in order to obtain the most rapid reaction. The greatest utilization of hydrogen would be obtained by the use of a counter current system of gas and bitumen flow in a series of autoclaves.

The optimum temperature is in the neighborhood of 380° C., which is considerably below the value of 425 (5, p. 226, 8) or more in the hydrogenation of coal and coal tar. The best catalysts are ammonium molybdate and aluminum chloride. Surprising as it appears, aluminum chloride has a favorable action in producing little gas and coke. It has the disadvantage of being corrosive and yielding an oil containing hydrogen chloride. The other catalysts are all definitely less active but as far as can be determined, have a beneficial effect. From the apparent rate of reaction, it might seem that the addition of a catalyst is hardly worth while. The time saved is small. However, the catalyst is very useful from the point of view of coke and gas production. These are invariably smaller when a catalyst is present, due no doubt to the greater rate of absorption compared to cracking in the initial stages of the reaction. The catalyst is probably largely removed ultimately by combination with sulphur and the over-all rate is not much improved by its presence. The catalysts have a further important advantage in permitting a lower working temperature. Cracking and wear and tear on the apparatus are minimized.

A comparison of hydrogenation with cracking experiments is of some interest in showing the difference in oil production. In Experiment 49, bitumen with no catalyst or gas, was heated to 400° C. for six hours in the closed autoclave. The maximum constant pressure was 1,600 lb. and the final cold pressure, 500 lb. The experiment yielded 103 litres of gas per kg. of bitumen, 35% coke and 51% oil. The oil was of good grade; density 0.886, viscosity 0.022, 38% unsaturated, initial boiling point 41° C., 68% boiling over at 300° C. A series of experiments on cracking in the presence of a high pressure of natural gas shows a great reduction in coke and gas production with a con-

sequent increase in oil yield. The coke production is approximately 20% and the gas from 10 to 50 litres per kg. bitumen. The Dubbs cracking process has been applied to the bitumen by Egloff and Morrell (6) at a pressure of 90 lb. per sq. in. The pressure distillate yield was 56%, the remainder being 42.3% coke, gas and tar, with 1.7% water. Egloff and Morrell estimate that 45 to 50% of the bitumen may be converted to N.E.P. gasoline of high anti-knock value.

The process of hydrogenation appears superior to cracking in virtue of the larger oil yield and smaller coke production. Gasoline yields cannot be compared until data on refining become available.

References

1. ALLAN, J. A. Research Council of Alberta, Reports 1 and 2. 1919-20.
2. ALLAN, J. A. Research Council of Alberta, Seventh Annual Report. 1926.
3. CLARK, K. A. and BLAIR, S. M. Research Council of Alberta, Report 18, Part I. 1927.
4. CLARK, K. A. and BLAIR, S. M. Research Council of Alberta, Report 18, Part II. 1927.
5. DUNSTAN, A. E. International Conference on Bituminous Coal 1:210-231. 1928.
6. EGLOFF, G. and MORRELL, J. C. The cracking of Bitumen from Alberta Tar Sands. Bulletin, Universal Oil Products Company, Chicago.
7. GILMORE, R. E., SWINNERTON, A. A. and CONNELL, G. P. Investigations of Fuels and Fuel Testing. Department of Mines, Canada. 83. 1927.
8. GRAHAM, J. I. The Hydrogenation and Liquefaction of Coal. Fuel 7: 543. 1928.
9. HUME, G. S. Oil and Gas in Western Canada. Geological Survey (Canada). 1928.

THE FORMATION OF ETHANE IN THE CATALYTIC DECOMPOSITION OF ETHYL ALCOHOL¹

BY E. H. BOOMER² AND H. E. MORRIS³

Abstract

The presence of ethane has been confirmed among the products of the catalytic decomposition of ethyl alcohol, and comparatively large amounts of carbon dioxide have been found to occur. The ethane produced has been shown to be due only in part, if at all, to the hydrogenation of ethylene, and may be explained by a decomposition of alcohol to acetaldehyde, water and ethane. In view of the small oil and acid production, the presence of carbon dioxide is inexplicable on the basis of accepted mechanisms.

Introduction

Ethane has been noticed among the products of the catalytic decomposition of ethyl alcohol and two mechanisms have been advanced to account for its presence.

Engelder (2) has suggested that it is due to the hydrogenation of ethylene, produced when using a catalyst that acts both in a dehydrating and dehydrogenating manner. If this is the case, it should be possible to demonstrate by gas analysis and water yields the truth of the suggestion. Dehydration yields ethylene and water; dehydrogenation yields acetaldehyde and hydrogen and as the temperature increases, the acetaldehyde will undergo further decomposition to methane and carbon monoxide. Part of the ethylene will be converted to ethane by some of the liberated hydrogen. The amount of dehydrogenation can be determined from these products and may then be compared with the actual hydrogen as determined by gas analysis. The amount of water produced will indicate the extent of dehydration and so the ethylene may be calculated. The ethylene determined by gas analysis plus the ethane as determined by gas analysis should equal the calculated value if the mechanism suggested by Engelder is correct.

The second mechanism suggested is due to Adkins (6) who proposes a reaction that yields ethane directly as follows:



With this mechanism, as the ethane yield increases, the water will also increase and determination of the latter will show which mechanism is correct.

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Experimental

The results reported below are part of a research on the catalytic decomposition of alcohol and water solutions conducted with special emphasis upon certain features largely neglected in previous work, i.e., the production of carbon monoxide, carbon dioxide and hydrogen.

The catalyst used in this particular set of experiments was prepared on a base of silica gel prepared after the method of Holmes and Anderson (3). The gel was allowed to set and then soaked in a concentrated solution of cupric and chromic chlorides in equimolar proportions. The gel was dried at 100° C., placed in the catalyst tube and treated with hydrogen for five hours at 300° C.

The apparatus employed was essentially the same as that used by others, with slight modifications of the method of Adkins and Nissen (1) for forcing the alcohol solution out of a graduated container into a vaporizer maintained at 105° C. The vapors passed through a vertical catalyst tube of pyrex glass fitted with a capillary exit tube to remove the products of reaction rapidly. Temperatures were measured by a platinum-rhodium thermocouple placed in a glass well embedded in the catalyst. Condensates were collected in a water-cooled receiver followed by a condenser in a solid carbon dioxide ether mixture. The gases passed through a flowmeter and a wet test-meter filled with mineral seal oil. The space-velocity was 0.15 cc. of water-alcohol mixture per minute.

The alcohol solution was made of water and alcohol in equimolecular proportions. It was found that the water had a depressing effect on the rate of reaction as reported by Engelder (2). Further, over this catalyst, the water took no part in the reactions and passed through the catalyst unchanged. Gas analyses were carried out on an improved Bureau of Mines apparatus; carbon monoxide and hydrogen being determined by combustion on copper oxide, methane and ethane by slow combustion with oxygen.

Experiments were made at 350°, 400°, 450° and 500° C. The gas analyses are given in Table I.

TABLE I
ANALYSIS OF GASEOUS PRODUCTS

Temperature in deg. C.	% H ₂	% CO	% C ₂ H ₄	% CO ₂	% CH ₄	% C ₂ H ₆
350	6.0	0.7	90.3	0.5	0.7	1.8
400	23.5	0.9	70.0	2.7	0.9	2.1
450	29.4	0.9	53.0	8.6	4.9	3.2
500	40.5	0.9	30.4	10.2	11.2	6.4

These results show quite clearly how the catalyst changed from a dehydration catalyst at 350° C., to one possessing considerable dehydrogenation powers at 500° C. It will be noticed that the percentage of ethane increased while that of the ethylene decreased. As the temperature is increased it is expected

that dehydrogenation will be favored (5). This would seem to indicate that the ethane was due to hydrogenation of ethylene, were it not for the fact that dehydrogenation is favored with rising temperature.

The analysis of the condensates was difficult and laborious. However, it was possible to determine the water with ease and a fair degree of accuracy. The water fraction was determined by fractional distillation in a 12-inch point and bulb column, any unchanged alcohol and aldehyde being sharply separated.

Discussion

The water actually produced by dehydration of alcohol decreased with increasing temperature as shown by the production of ethylene. This decrease is not as great as would be expected if the water were all formed by dehydration of alcohol to ethylene. The extra quantity of water produced can be accounted for in part by assuming the reaction as suggested by Adkins (6) to occur at the higher temperatures. Table II gives a summary of the calculated quantities of water and the measured quantities as found by experiment.

TABLE II
CALCULATED AND EMPIRICAL QUANTITIES OF WATER FORMED

Temperature, in deg. C.	350	400	450	500
Volume of alcohol solution, in cc.	36.4	29.9	8.3	29.6
Condensate, in cc.	23.5	20.0	7.0	12.0
Alcohol decomposed, in cc.	12.9	9.9	1.3	17.6
Water from alcohol solution, in cc.	7.3	6.0	1.7	5.9
Water from dehydration, based on ethylene, in cc.	3.8	2.4	0.2	3.1
Water, calculated on ethane formation, in cc.	0.1	0.1	0.1	0.7
Total calculated water, in cc.	11.2	8.5	2.0	9.7
Water found, in cc.	11.5	8.7	2.5	10.2
Positive error, in cc.	0.3	0.2	0.5	0.5

It was noticed, in agreement with other work, that all of the condensates were acidic in nature and on distillation yielded a minute quantity of brown odorous oil. The acid distilled with the water fraction, but due to the small quantities present its identification has not been accomplished. It is possible that this acid may account for the invariable excess of water found over the calculated quantity.

The origin of the oil produced is problematical and may be due to reaction of acetaldehyde and a ketene to produce carbon dioxide and an unsaturated hydrocarbon as suggested by Lazier and Adkins (4). However, it is doubtful if anything can be said on this point from the experiments reported. The quantities of carbon dioxide produced are so large that some doubt is cast on the above mechanism for its origin. Carbon is not deposited on this

catalyst and carbon monoxide cannot be considered as the origin of the carbon dioxide. Related work on other catalysts, which produce even more carbon dioxide and at lower temperatures, indicates a necessity for another explanation to be discussed in a subsequent paper.

References

1. ADKINS, H. and NISSEN, B. H. *J. Am. Chem. Soc.*, 46:130-145. 1924.
2. ENGELDER, C. J. *J. Phys. Chem.*, 21:676-704. 1917.
3. HOLMES, H. N. and ANDERSON, J. A. *Ind. Eng. Chem.*, 17:280-282. 1925.
4. LAZIER, W. A. and ADKINS, H. *J. Am. Chem. Soc.*, 46:2291-2305. 1924.
5. PEASE, R. N. and DURGAN, E. S. *J. Am. Chem. Soc.* 50:2715-2718. 1928.
6. TAYLOR, H. S. *J. Phys. Chem.*, 30:145-171. 1926.

THE DENSITY OF CARBON DIOXIDE¹

By D. LeB. COOPER² AND O. MAASS³

Abstract

Modifications are described by the Maass and Russel method for the determination of the densities of gases which permit an accuracy of about one part in 10,000. The determination has been made of the density of carbon dioxide at two temperatures and over a pressure range of 75 to 25 cm. of mercury. The mean value obtained for the molecular weight of carbon dioxide at zero pressure is 44.0033 ± 0.002 , from which the atomic weight of carbon is found to be 12.0033 ± 0.002 .

Introduction

Especial interest is attached to the density of carbon dioxide, because equations of state have been built up on data connected with this compound since Van der Waal used the data of Amagat.

The density of carbon dioxide has been the subject of many investigations both at high and low pressures. Considerable accuracy was attained by Maass and Mennie (8) in determinations over a temperature range from -70° C. to 200° C., and at pressures below one atmosphere. Equations of state have been developed, which represent the experimental values hitherto obtained, within the accuracy of the determinations. It is hoped that the further increase in accuracy* of the results presented in this paper will help to throw more light on the deviations from the ideal gas laws.

The many determinations of the atomic weight of carbon, both physical and chemical, discussed by Birge (2), Moles (9), Clarke (3) and others, appear to leave little to be desired in the determination of this constant. The values obtained by Guye (5) and others, with the exception of Aston (1), by physical methods, depend, however, on an equation containing several constants deduced, in part, from other gases; they may or may not hold for carbon dioxide. The close agreement between the physical and chemical methods argues well for the validity of the Guye (5) equation, but up to the present time no data of sufficient accuracy to allow a direct extrapolation for the atomic weight of carbon have been obtained. Such results are included in this paper.

Preparation of carbon dioxide

The carbon dioxide used in the experiments was prepared by dropping pure phosphoric acid on pure anhydrous potassium carbonate. After generation, the gas was condensed into two storage bulbs by a known method (8), and

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² Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, with financial assistance from the National Research Council.

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* This paper is to be considered of a preliminary nature even with respect to the results concerning carbon dioxide. A programme of work has been arranged which entails the repetition of the present determination; this may necessitate corrections which will be published at a later date.

pumped free of air by several partial evacuations at its sublimation point. The amount of air remaining in the carbon dioxide could be estimated from the residual pressure; in cases where this was above approximately 0.20 cm. of mercury the gas was discarded.

The gas was analyzed for chlorine and sulphur dioxide: it showed no trace of either.

Apparatus

For the calculation of the apparent molecular weight from the ideal gas equation, four measurements are necessary, i.e., volume, temperature, pressure, and weight. These measurements necessitated four separate sections in the apparatus, which, for convenience, will be discussed separately.

(a) Measurement of volume

The constant volume bulb, constructed of pyrex glass of approximately 5.5 l. capacity, was standardized in the usual manner by weighing with water. With all corrections applied the volume at 20.7° C. was $5442.85 \pm .05$ ml., using .997638 as the absolute density of water in gm. per ml. at 20.7° C. When in use at temperatures other than that of standardization, the new volume of the bulb was calculated from the equation of Keyes (6).

(b) Measurement of pressures¹

Pressures were read on mercury manometers, built of pyrex glass tubing of 15 mm. diameter, so constructed that the two menisci lay in the same vertical plane. This arrangement necessitated no rack motion of the cathetometer telescope, except in the reading of the comparatively small residual pressures. Corrections for differences in the heights of the menisci were in all cases negligible. The differences in the heights of the mercury columns were measured on a cathetometer scale with a vernier reading to 0.001 cm., the bar of which was compared against a standard meter bar. With the cathetometer telescope at a distance of 18 cm. from the manometers, the sensitivity of the bubble of the telescope enabled a difference of 0.001 cm. to be detected.

The carefully cleaned manometers, filled with thrice distilled mercury were enclosed in a constant temperature bath, and the temperature correction for each difference in height calculated.

(c) Measurement of temperatures

The constant volume bulb was placed in a well-lagged metal bath filled, at the higher temperature, with water, and at the lower temperature with a solution of sodium chloride in water. At the higher temperature the bath was thermostatically controlled, and the temperature read on a calibrated thermometer to $\pm 0.01^\circ$ C. At the lower temperature the bath was hand regulated, and the temperature read from a Beckmann thermometer, the ice point of which had been determined in a Beckmann freezing point apparatus. At the lower temperature the bath could be kept constant to $\pm 0.003^\circ$ C.

(d) *Determination of mass*

Considerable attention was given to proper methods of weighing, since it is in this particularly that the method offers greater advantages than any other.

After having been sealed off, the small especially constructed pyrex bulbs of 20 and 10 cc. capacity were placed, while still cold, in a small basket-holder constructed of very thin pyrex glass rod. This was suspended in the centre of a box, and connected to the balance pan by a thin rod of glass, held by a small loop of wire soldered to the bottom of the pan. The box was lined with copper, and the lining grounded. The air inside the box was always kept at constant humidity, by a current of pure dried air which had been passed through sulphuric acid, phosphorus pentoxide, and finally through a small tube of uranium nitrate, to remove any charge on the glass. Equilibrium was established in from three to six hours, depending on the size of the bulbs, and single weighing could be repeated to 0.00005 gm. The small uncertainty in the weighings is due to the method of opening the bulbs, which however allowed repetition to ± 0.0003 gm. Other methods of opening were tried but were not successful.

The apparatus and procedure

The apparatus was set up as shown in Fig. I (not drawn to scale) which is self explanatory. It was constructed of pyrex glass. The dead space between B and G varied between 70 and 120 cc. depending on the number and size of the bulbs sealed on the apparatus. In most cases, the correction for the amount of contained gas in this dead space was negligible.

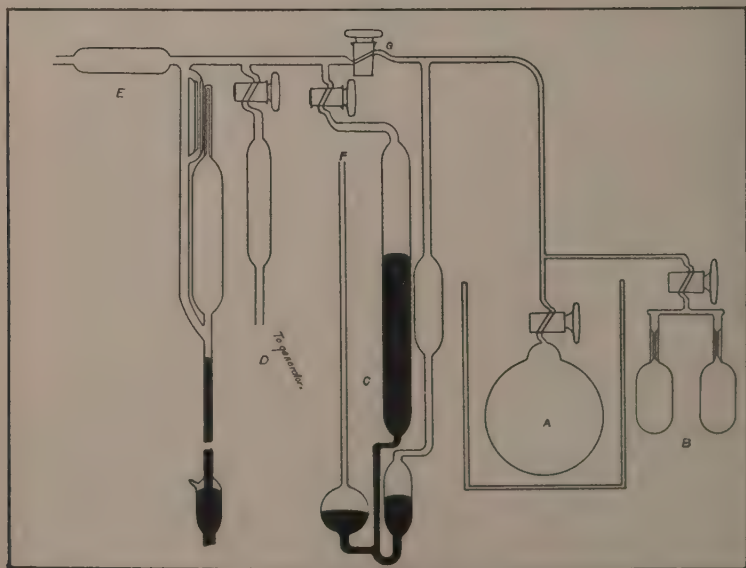


FIG. 1. *Diagram of apparatus used*

Experiments were carried out as follows. The carbon dioxide in the storage bulbs was pumped free of air, and allowed to expand into the apparatus to the desired pressure. The constant volume bulb, connection tubing, and other parts of the apparatus had been previously pumped out to a pressure of 1×10^{-4} mm. of mercury, and flushed out several times with pure carbon dioxide. After the gas had reached the desired pressure the dead space was shut off, and the levels of the mercury manometer adjusted to the desired position by applying a vacuum or pressure at F. The constant temperature bath was then adjusted.

The gas was allowed to remain in the constant temperature bath until two or three readings at intervals of five minutes showed that it had reached thermal equilibrium; this usually required about 15 min.

Pressures having been recorded, the temperature of the manometer bath and the cathetometer scale were read, the constant volume bulb was closed and the dead space evacuated. The dead space was again closed, and the gas condensed into the weighing bulbs with liquid air. These bulbs were sealed off and weighed; they were then cut open, blown out with air, reweighed, and finally weighed with water to determine their volume.

Subsequent to the sealing off of the bulbs, the small residual pressure was determined, and this subtracted from that first observed.

It may be well to emphasize once more the special feature of this method, namely, that the dead space is completely evacuated after the constant volume bulb has been filled; since the residual pressure after condensation is very small, the dead space error is completely eliminated.

Discussion of errors

In this discussion the "precision measure of the mean", as defined by Goodwin (4), is used.

The calculations which are given show the agreement that could be expected between any two similar experiments, and also the precision measure of the means, determined in sets of experiments.

All sections of the apparatus were tested for instrumental errors and the agreement between the two calculations shown below increases the confidence that all constant errors have been eliminated.

Granted the following deviations, which were determined from an inspection of the results obtained, and from specially designed experiments, i.e.,

T , in degrees absolute	$\pm .01$
w , in grams	$\pm .0003$
P , in cm. of Hg (45° lat.)	$\pm .006$
V , Deviation negligible,	

the following precision measures are calculated for errors in M' .

	Temp. = 24° C.	Temp. = 0° C.
75 cm. of Hg	$\pm .0041$	$\pm .0034$
50 cm. of Hg	$\pm .0057$	$\pm .0050$
25 cm. of Hg	$\pm .011$	$\pm .0093$

For the mean values, the following hold:

	Temp. = 24° C.	Temp. = 0° C.
75 cm. of Hg	±.0017	±.0016
50 cm. of Hg	±.0017	±.0014
25 cm. of Hg	±.0018	±.0020

A further discussion will be found in the section on experimental results.

Experimental Results

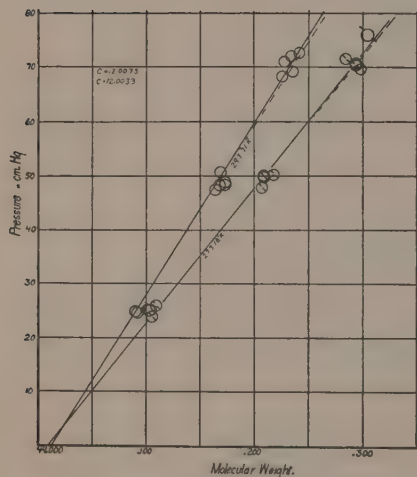


FIG. 2. Function of the molecular weight to the pressure.

The results are shown in Tables I and II and Fig. 2 and 3. The last column in the tables shows the apparent molecular weight M' calculated from the equation,

$$PV = \frac{W}{M'} RT$$

that is, M' is the molecular weight of an ideal gas which would satisfy the pressure, volume, weight, and temperature, of the experiment.

Calculations were made as shown below.

Temperature of manometer bath 19.17, 19.20° C.

Temperature of cathetometer bar 22.3, 22.5° C.

Original pressure, 70.578, 70.572; mean = 70.575.

Residual pressure .023, .024, .021; mean = .0223.

Temperature of constant volume .004° C., 273.18° A.

Wt. of CO₂, uncorrected, 9.9305.

Volume of tube 20.044 cc. at 19.2° C. and 74.8 cm. of Hg.

Correction for temperature of manometers, 0.215; net pressure, 70.338.

Volume of dead space 90 cc.

Wt. of gas in dead space .00004 gm.

Correction for weight of air in bulb

.0293 gm.

Correction for air displaced by brass weights

.0013 gm.

Correction for gas contained in dead space

negligible

Net weight

= 9.9530 gm.

$$M' = \frac{9.9530 \times 0.082048 \times 273.18 \times 760}{70.338 \times 5441.6} = 44.295.$$

TABLE I
RESULTS OF EXPERIMENTS

Pressure, in cm. of Hg.	Temperature, $T = 273.18$	Weight, in gm.	Volume, in ml.	Molecular, weight M'
75.424	297.71	9.7852	5442.8	44.250
72.769	297.73	9.4385		44.242
72.363	297.76	9.3827		44.234
71.165	297.73	9.2274		44.228
69.363	297.72	8.9956		44.236
68.400	297.72	8.8689		44.226
47.467	297.61	6.1486		44.164
48.036	297.59	6.2233		44.170
48.475	297.62	6.2801		44.173
48.991	297.59	6.3474		44.173
50.681	297.70	6.5633		44.169
25.366	297.69	3.2803		44.102
25.293	297.71	3.2706		44.104
25.082	297.71	3.2436		44.107
25.201	297.54	3.2597		44.103
25.015	297.54	3.2355		44.090
24.907	297.71	3.2211		44.110
24.810	297.74	3.2070		44.092
24.609	297.71	3.1824		44.109

TABLE II
RESULTS OF EXPERIMENTS

Pressure, in cm. of Hg.	Temperature, $T = 273.18$	Weight, in gm.	Volume, in ml.	Molecular weight M'
71.761	273.11	10.1569	5441.62	44.294
70.338	273.18	9.9530		44.294
70.163	273.18	9.9267		44.287
69.690	273.18	9.8617		44.297
50.229	273.06	7.0968		44.218
59.049	273.13	7.0693		44.209
49.826	273.11	7.0379		44.209
47.960	273.18	6.7727		44.207
26.128	272.92	3.6851		44.109
24.332	273.18	3.4306		44.136
24.028	273.18	3.3853		44.106

The following method was used for the determination of the true molecular weight of carbon dioxide at zero pressure. Examination of the curves of Fig. 2 shows that the function of the molecular weight to the pressure may be represented by a straight line, making it possible to correct all experimental molecular weights to one definite pressure which was usually taken as the mean of those observed. The means calculated are shown in Table III.

TABLE III
CALCULATED VALUES OF THE MOLECULAR WEIGHT
Corrected values at 0° C.

Pressure	M'
72.0	44.2922 ± .0017
50.0	44.2125 ± .0017
25.0	44.1025 ± .0018

These values are shown plotted in Fig. 3. From the curve the molecular weight of carbon dioxide at zero pressure is read:

$$44.0033 \pm .002$$

which gives for the atomic weight of carbon

$$12.0033 \pm .002$$

The following constants have been used in the calculations:

Temperature of the ice point	273.18 ± .03 K.
The gas constant <i>R</i>	.082046 l. at deg ⁻¹ mol ⁻¹ .
Constant of gravity	980.616 cm. sec ⁻² .

Discussion of results

It will be noticed that in the value calculated for the atomic weight of carbon the 24° C. curve was not considered. There is still some slight doubt about the 25 cm. point on this curve, due to the presence of a suspected constant error. The curve is therefore omitted entirely but will be repeated in later work.

On the whole the points fall sufficiently well within the limit of calculated error which was based on the physical measurements only, and could not take into account the effect of any possible impurities in the gas. Hence, the facts that the points are so satisfactory, and that every precaution to prevent impurities was taken, are good indications that the gas was free from the latter.

Inspection of the results obtained by Maass and Mennie (8) shows that their values agree with those given above well within the limit of their calculated experimental error, both on the zero and 24° C. curve. Their curves are shown as dotted lines in Fig. 2.

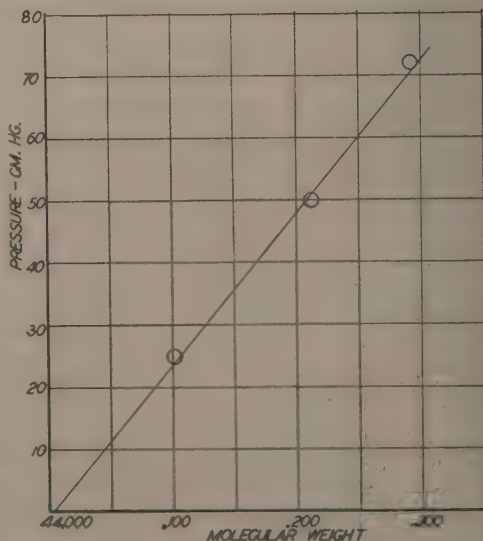


FIG. 3. Function of pressure to calculated mean values of the molecular weight.

The value of the molecular weight at 0° C. and 760 mm. pressure agrees very well with that obtained by Guye (5), (calculated from the weight of a normal litre).

The molecular weight of any gas which it is possible to treat in the manner described above, may be determined very simply by using an oil manometer whereby a value of M' at 3 cm. of mercury may be obtained without loss of accuracy. It is the intention of the authors to investigate this method of attack.

Acknowledgment

The authors wish to express their appreciation to Mr. E. O. Way, and his staff, at the Department of Weights and Measures in Ottawa, for their permission to use the Departmental balances and weights in standardizing the large volume, and for their very generous assistance while the work was in progress.

References

1. ASTON, F. W. *Proc. Roy. Soc. A*, 115: 487-514. 1927.
2. BIRGE, R. T. *Phys. Rev. Supp.* 1: 1-73. 1929.
3. CLARKE, F. W. *A Redetermination of Atomic Weights.* 4th ed. 1920.
Proc. Nat. Acad. Sci. Part 3, Vol. 16.
4. GOODWIN, H. M. *Elements of the Precision of Measurements, and Graphical Methods*, 2nd ed. 1920.
5. GUYE, P. A. *J. chim. phys.* 4: 174-185. 1906.
6. KEYES, F. G., TAYLOR, R. S. and SMITH, L. B. *J. Math. Phys., Mass. Inst. Tech.* 1: 211-242. 1922.
7. MAASS, O. and RUSSEL, J. *J. Am. Chem. Soc.* 40: 1847-1852. 1918.
8. MAASS, O. and MENNIE, J. H. *Proc. Roy. Soc. A*, 110: 198-232. 1926.
9. MOLES, E. *Rec. trav. chim.* 48: 864-871. 1929.

ASTROPHYSICAL DATA FROM EASTERN CANADA¹BY A. BROOKER KLUGH² AND W. REGINALD SAWYER³

Abstract

On account of investigations on the effect of light on various marine and fresh-water organisms which are being carried on at the Atlantic Biological Station, St. Andrews, N.B., Canada, it was necessary to know something of the energy values of sunlight, especially of its ultra-violet component, and also of moonlight. Consequently a Moll-Richard-Gorczyński pyrheliometer, and various other apparatus for measuring natural radiation, were brought into use in the summer of 1926. It was found that the sun, shining from a clear sky in June at this Station (Lat. 45° N. sea-level) had an energy value of 1.55 gm. cal. per sq. cm. per min., and data on the effects of clouds and haze were obtained. The ultra-violet component of the sun's radiation was found to be 2% of the total radiation in August. The energy value of the light of the full moon, at an elevation of 22° above the horizon in July was found to be 0.0000029 gm. cal. per sq. cm. per min., or about 1/555,000 that of full noon June sunlight.

During the past five years several research workers at the Atlantic Biological Station have been investigating the effect of light upon various marine and fresh-water organisms. The great majority of these investigations have been carried on with daylight (sunlight and skylight) as a source of illumination, because it was realized that any artificial illumination which might be employed would vary so much in spectral distribution from the light received by organisms in their environments, that no data obtained by the use of artificial illumination could have any direct application to natural conditions.

On account of the fact that sunlight was used in these experiments it was essential to procure data on the energy values of the sunlight which was received at this Station during the course of the experiments and especially upon the values of the ultra-violet component of sunlight; because in some of these experiments it was with the effects of ultra-violet radiation that we were particularly concerned. Data on the energy values of sunlight could not be obtained from meteorological stations, because no station in Canada has a pyrheliometer in operation. Consequently in the summer of 1926 a Moll-Richard-Gorczyński pyrheliometer was brought into use; this instrument, described by Gorczyński (8), was obtained from Messrs. Jules Richard, Paris. It was calibrated in gm. cal. per sq. cm. per min. by l'Institut de physique du globe, Université de Paris. A continuous record not being necessary, but instantaneous readings made in quick succession being needed, the recording mechanism provided with the instrument was not used, but the readings as indicated by the deflection of the galvanometer pointer were recorded. With this instrument and accessory

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apparatus, during the summer months of the past three years, we have secured considerable information on solar radiation at the Station, especially in regard to total irradiation at different hours of the day and in different weather conditions; we have also determined the ultra-violet component of the sun's radiation. Because of the lack of such observations in Canada it seems desirable to publish some of this data.

Total Energy Value of Sunlight

The highest value ever obtained in these experiments was 1.61 gm. cal. per sq. cm. per min. which was recorded at noon, June 22, 1926. In this case the sun shone perfectly clearly between two masses of cumulus clouds, and this high value was unquestionably due to what has been termed "axial reflection", to which reference is being made below.

The highest value obtained for the sun shining from a clear sky was recorded on June 24, 1927, and the record for this day is as follows:

7.45 A.M.—1.36 gm. cal. per sq. cm. per min.	
9.00 A.M.—1.47 " " " " " "	
10.45 A.M.—1.55 " " " " " "	
11.15 A.M.—1.57 " " " " " "	
12.00 M. —1.57 " " " " " "	
12.30 P.M.—1.55 " " " " " "	
1.00 P.M.—1.55 " " " " " "	
2.30 P.M.—1.10 " " " " " "	Cirrus clouds
3.00 P.M.—1.12 " " " " " "	"
4.10 P.M.—1.06 " " " " " "	"
5.15 P.M.—1.14 " " " " " "	Clear sun
6.15 P.M.—0.85 " " " " " "	"
7.15 P.M.—0.35 " " " " " "	"

The sun may appear as bright on one day as on some other day and yet have a very different energy value, due to more water vapor in the air. This has been proved in subsequent work in which a sling psychrometer was used for measuring humidity at the time the irradiation records were taken. The record taken on June 27, which is an example of such a day, is as follows:

7.45 A.M.—1.32 gm. cal. per sq. cm. per min.
8.45 A.M.—1.34 " " " " " "
9.45 A.M.—1.36 " " " " " "
10.15 A.M.—1.36 " " " " " "
11.45 A.M.—1.41 " " " " " "
1.45 P.M.—1.40 " " " " " "
3.15 P.M.—1.40 " " " " " "

From a large number of observations made during the past four years, it can be stated that on clear days with low humidity the usual highest value at Latitude 45° N., sea-level, in June and early July, is 1.55 gm. cal. per sq. cm. per min. Later in the season this value is never reached, and a typical clear August day (August 16, 1926) had the following record:

8.00 A.M.—1.11	gm. cal. per sq. cm. per min.	
8.15 A.M.—1.13	" " " " " " "	
8.45 A.M.—1.26	" " " " " " "	
9.15 A.M.—1.27	" " " " " " "	
10.00 A.M.—1.28	" " " " " " "	
11.00 A.M.—1.25	" " " " " " "	Slight cirrus haze
11.30 A.M.—1.34	" " " " " " "	
1.00 P.M.—1.25	" " " " " " "	
3.30 P.M.—1.11	" " " " " " "	Cirrus haze
4.00 P.M.—1.17	" " " " " " "	
4.30 P.M.—1.05	" " " " " " "	
6.30 P.M.—0.31	" " " " " " "	
7.00 P.M.—0.21	" " " " " " "	

On days when there is considerable cirrus haze so that the sunlight is faint and yet sufficiently strong to cause objects to cast slight shadows the energy values range from 0.44 to .062 gm. cal. The record for such a day (July 27, 1926) is as follows:

8.30 A.M.—0.49	gm. cal. per sq. cm. per min.
10.00 A.M.—0.56	" " " " " " "
10.30 A.M.—0.60	" " " " " " "
12.00 M. —0.60	" " " " " " "
1.00 P.M.—0.60	" " " " " " "
2.30 P.M.—0.60	" " " " " " "
4.00 P.M.—0.49	" " " " " " "
5.00 P.M.—0.31	" " " " " " "

Cumulus clouds, when they come across the sun, cut down the irradiation so greatly that its energy value is below the sensitivity of the galvanometer of the instrument, so that no measurements can be made.

When, however, there are heavy cumulus clouds close to the sun, but not obscuring it in the slightest degree, the increase in the energy value, to which reference has been made, is observed. This fact has been noticed again and again in the course of the measurements, and, as an example the following records taken on August 3, 1928, are given:

Sky clear around sun	Clouds near sun
1.25 gm. cal. per sq. cm. per min.	1.34 gm. cal. per sq. cm. per min.
1.25 " " " " " " "	1.30 " " " " " " "

This phenomenon the authors have called "axial reflection" because the extra energy received by the thermopile of the pyrliometer seems to be due to multiple reflection from the faces of the clouds which are nearest the sun and the direction of some of this along the axis from the sun to the opening in the pyrliometer diaphragm system.

Determination of the Ultra-violet Component of the Sun's Radiation

For the purpose of experiments on the effects of natural ultra-violet light on organisms it was essential to know the value of the ultra-violet component of the sun's radiation, that is, what percentage of the energy of sunlight lies in the spectral region from $400\text{ m}\mu$, the end of the visible spectrum, to $289\text{ m}\mu$, the shortest wave-length which penetrates the earth's atmosphere. As far as we know, the literature on solar radiation does not give the required information, and as may be seen from the following brief review there is a wide divergence in the data presented by different workers.

Fowle (6, table 175) gives a value for wave-lengths $0\text{--}450\text{ m}\mu$ of $0.13\text{ gm. cal. per sq. cm. per min.}$ for air mass of one and of 0.06 gm. cal. for air mass of two at Washington. Total radiation is given for air mass of one as 1.35 gm. cal. , so that the region $0\text{--}450\text{ m}\mu$ contains 9.6% of the total. The air mass at noon at St. Andrews ranges from 1.08 in June to 1.27 at the end of August. In Fowle's Table No. 174, in which solar radiation at Washington for an air mass of one is given in arbitrary units for various wave-lengths from $380\text{ m}\mu$ to $2,000\text{ m}\mu$, it is found that the amount of energy from $380\text{ m}\mu$ to $400\text{ m}\mu$ is 5.5% of the total.

Dorno (4) gives transmission coefficients for wave-lengths $402\text{ m}\mu$ to $308\text{ m}\mu$ for Potsdam (after Kron) and $400\text{ m}\mu$ to $285\text{ m}\mu$ for Teneriff (after Dember), and some results on the variation of ultra-violet with altitude, the sun's elevation, and the seasons, but no energy or percentage values. Luckiesh (15) quotes Fowle's results.

Coblentz and Kahler (1), using a spectropyrheliometer, made measurements of solar radiation at Washington on September 13, 16, 24 and 25, 1919. They divided the spectrum into three regions—from 750 to $3,000\text{ m}\mu$, from 389 to $750\text{ m}\mu$, and from 300 to $389\text{ m}\mu$,—and found that at noon 1.09% to 2.16% of the total energy lay in the latter region.

Coblentz, Dorcas and Hughes (2) state that the region from $170\text{ m}\mu$ to $320\text{ m}\mu$ contains 1.8% , and the region from 320 to $370\text{ m}\mu$ contains 3.2% of the total radiation of the sun at Washington in June at 11 A.M.

Fabry and Buisson (5) show how the shorter wave-lengths of the ultra-violet (from $292\text{ m}\mu$ to $294\text{ m}\mu$) decrease towards the beginning and end of the day as compared with the hours near midday.

Petit (16) says that the energy value of the region from $290\text{ m}\mu$ to $310\text{ m}\mu$ at Mt. Wilson (altitude $1,780\text{ m.}$) is $0.7\text{ watts per square metre}$, which is equal to $0.001\text{ gm. cal. per sq. cm. per min.}$ His measurements show that the value of the ultra-violet radiation of wave-length $320\text{ m}\mu$ has varied over 50% in four years and he states that the variation at $300\text{ m}\mu$ is probably 20% greater than that at $320\text{ m}\mu$. He shows that the curve for wave-length $320\text{ m}\mu$ is very similar to that for the number of sun spots. Petit has also measured the value for this radiation received on a horizontal surface from the sky and states that it is as much as that received from the sun, and, further, that in certain kinds of hazy weather the sky may radiate nearly twice as much ultra-violet as the sun on a clear day.

Hulburt (10) gives a table of the energy of the sun's ultra-violet of various wave-lengths which is absorbed by the earth's atmosphere, and Dawson, Granath and Hulburt (3) show that for wave-lengths less than 280 $m\mu$ there is pronounced absorption by the lower atmosphere.

The method of determining the ultra-violet component of the sun's radiation which was adopted in 1927 is as follows:

A spectroscopic cell was constructed with one wall made of Corning glass No. G986A and the other of Corning glass No. 980A (3). The former is a red-purple glass which transmits from wave-length 408 $m\mu$ to 250 $m\mu$ with a transmission of 50% at wave-length 380 $m\mu$, 80% at wavelength 340 $m\mu$ and 65% at wave-length 300 $m\mu$. This glass also transmits the extreme red from 720 to 760 $m\mu$, and it was found that the red component was 75% of the total energy transmitted by a plate of this glass 4 mm. thick. The second glass, No. 980A, is clear, and a sheet, 2 mm. thick, transmits both the visible spectrum and the ultra-violet as far as 220 $m\mu$. This cell was 14 mm. deep and twice as great in diameter as the opening in the screen system of the pyrliometer. The cell was filled with a solution of copper sulphate and it was found, by taking spectrograms through the cell with a Hilger quartz spectrograph, that a 10% solution completely absorbed the red which passed through the G986A filter.

The transmission of the cell filled with 10% copper sulphate for the ultra-violet of the sun was then determined in the following manner. An exposure of 10 sec. was given a plate in an instrument designed to record the effect of ultra-violet and the extreme violet as far as wave-length 430 $m\mu$, which is described by Klugh (14). This exposure was made with the instrument pointing directly at the sun, which was shining from a clear sky, and had a value of 1.28 gm. cal. per sq. cm. per min. at 12.40 p.m. on August 6. The cell was then placed between the sun and the instrument and a series of exposures of 14, 15, 16, 17, 18, 19, 20, 21 and 22 sec. was taken. When the plates were developed the 10-second exposure to direct sunlight was equal in density to the 19-second exposure through the cell, so that the transmission of the cell for ultra-violet of wave-lengths 289 to 408 $m\mu$ was 10/19 or 52%. This method of calibration involves the use of the reciprocity law ($E = I.t$) only to two times, and it had been found previously by experiment that the plates used showed no discernible deviation from this relationship for exposures up to five times.

On August 22 a series of readings with this cell over the opening of the diaphragm system of the pyrliometer gave the value for the ultra-violet component of a clear sun of 2.26%.

Owing to the fact that the galvanometer of the pyrliometer gave such very small deflections when the ultra-violet only was allowed to reach the thermopile the reliability of the readings was not regarded as being satisfactory, and in 1929 a suspension type galvanometer was brought into use which, when used with a shunt, had a sensitivity 10 times as great. By this time the Corning Glass Works had originated several new optical glasses (7) and one of

these, known as Ultra-light Blue Green absorbs the red passed by the G986A filter—a fact stated by Gage (7) and confirmed by the authors' spectrographic determinations. Hence it was possible to use this filter in combination with the G986A filter and thus avoid the use of the copper sulphate solution which by reason of its extremely corrosive nature is decidedly objectionable.

In 1929 not only was the use of a glass filter adopted to remove the red component of the G986A filter, but a different method of determining the transmission of the filter system was used. We determined the transmission by obtaining the transmission of a combination of two G986A filters and two Ultra-light Blue Green filters, as shown by the pyrheliometer with the suspension galvanometer, and the transmission of the combination of one of each of these filters, and subtracting the value obtained for the latter from that of the former. Also the infra-red component of the G986A plus the Ultra-light Blue Green combination was determined by the use of a Wratten No. 88 (infra-red) filter, and found to be 33%; it was thus concluded that the readings obtained with this combination, when multiplied by a factor of 1.4, gave a true value for the ultra violet.

Determinations made on August 21, 1929 on the sun shining from a clear sky and an energy value of 1.23 gm. cal. per sq. cm. per min. with this filter combination gave a value for the ultra-violet component of 2.03% of the total solar radiation.

The Effect of Clouds on the Ultra-violet Radiation of the Sun

Clouds, both cirrus and light cumulus clouds, over the sun cut down the ultra-violet much less than they do the total radiation. This matter was investigated both in 1927 and in 1929. Some results obtained on August 22, 1927 are as follows:

Clear sun.	Total 1.21 gm. cal.	Ultra-violet 2.2%
Cloud over sun.	T. 1.13 gm. cal.	Ultra-violet 2.5%
Cloud over sun.	T. 0.82 gm. cal.	Ultra-violet 3.9%
Cloud over sun.	T. 0.43 gm. cal.	Ultra-violet 4.7%.

Determination of the Energy Value of Moonlight

Since moonlight was found to have an influence on the bathymetric distribution of some marine organisms, especially of certain species of Copepods, it was desired to learn something of the energy value of the moon's radiation. By the use of an instrument known as the Ecophotometer which was originated by one of the authors (11, 12, 13) and which was calibrated in gm. cal. per sq. cm. per min., it was ascertained that the light of the full moon, at an elevation of about 22° above the horizon, at 11 p.m. on July 24, 1926, had a value of 0.0000029 gm. cal., or about 1/555,000 of full noon June sunlight.

References

1. COBLENTZ, W. W. and KAHLER, H. Sci. Papers, U.S. Bur. Standards. No. 378. 1920.
2. COBLENTZ, W. W., DORCAS, M. J. and HUGHES, C. W. Sci. Papers, U.S. Bur. Standards. No. 539. 1926.
3. DAWSON, L. H., GRANATH, L. P. and HULBURT, E. O. Phys. Rev. 34:136. 1929.
4. DORNO, C. Physik der Sonnen-und Himmelstrahlung. 1919
5. FABRY, C. and BUISSON, H. J. phys. radium. [6] 2:197. 1921.
6. FOWLE, F. E. Smithsonian Physical Tables. 1913.
7. GAGE, H. P. J. Optical Soc. Am. 17:40-42. 1928.
8. GORCZYŃSKI, L. J. Optical Soc. Am. 9:455-464. 1924.
9. HOOD, H. P. Science. n.s. 64:281. 1926.
10. HULBURT, E. O. Phys. Rev. 31:1018. 1928.
11. KLUGH, A. B. Ecology. 6:203. 1925.
12. KLUGH, A. B. Ecology. 8:174. 1927.
13. KLUGH, A. B. Ecology. 8:415. 1927.
14. KLUGH, A. B. Ecology. (In the press.)
15. LUCKIESH, M. Ultra-violet Radiation. 1922.
16. PETIT, E. Trans. 24th Ann. Meeting Nat. Tuberculosis Assn. 110-118. 1928.

THE UDDER AS A RESERVOIR OF *BR. MELITENSIS* (*ABORTUS*) INFECTION OF CATTLE¹

BY CHAS. A. MITCHELL² AND R. C. DUTHIE³

Abstract

The removal of the udders from two cows known to be infected with *Br. melitensis* (*abortus*) was followed in both cases by a reduction in agglutination titre. In the one case, the agglutination titre declined from 1:600 to a value within the negative range, 1:25, and in the other the very high agglutination titre (1:28000) rapidly declined to a point just within the positive range, 1:100.

Introduction

It is perhaps regrettable that the name infectious abortion should have been chosen to indicate infection in certain animals by *Br. melitensis* (*abortus*). Although this name serves to emphasize the principal symptom, it forces into the background other factors of importance. Moreover, it tends to fix in the lay mind the impression that abortion is necessarily an accompaniment of infection, and that if normal gestation is resumed the infection has cleared up.

The udder was early discovered to be a source of organisms in infected animals. Smith (3) and Schroeder (1), working separately, each drew attention to the presence of the *Br. melitensis* (*abortus*) in the udder. Since then, Schroeder and Cotton from time to time have focussed attention on udder infection. Of particular interest was the observation that the uterus only temporarily harbored organisms, and that a few weeks following delivery, infection of this organ apparently cleared up (2). The authors' experiments have confirmed this, and have shown that even in oestrus the infected animal does not harbor the organism in the uterus.

In common with others, the present authors have also found that in a large proportion of infected animals, *Br. melitensis* (*abortus*) is harbored in the udder, but not necessarily by each quarter.

It is therefore pertinent to consider what part udder infection plays in the whole picture; also whether the udder is the seat of a focal infection harboring organisms when the animal is not pregnant, and permitting of the distribution of organisms to the placental tissues during pregnancy. If such were true, it would considerably alter present views on the infection, and perhaps open a new avenue for attacking the problem.

Cow No. 132

Experimental

This animal was two years old and in her 228th day of first pregnancy. Agglutination tests prior to December 1928 were negative (1:10). Then she reacted positively to the agglutination test with a titre of 1:100, which titre

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gradually increased until at the date of operation (April 29, 1929) it reached 1:600. On April 29 the animal was placed under general anaesthesia, and the udder and supramammary lymph glands were removed surgically. Each of these tissues was ground and inoculated into guinea pigs. The guinea pigs inoculated from the udder became infected, while those from the supramammary glands showed no evidence of infection.

After a rather stormy period due to shock and some trouble from infection, the animal made a very good recovery. It may be worth recording that the use of a 5% hypochlorous acid solution was found to be a most efficient application to the wound caused by the operation, and not until this solution was used was it possible to control post-operative infection and sloughing.

On May 14, the cow aborted, and from the foetus and washings from the uterus *Br. melitensis (abortus)* was isolated.

A study was undertaken of the blood serum to determine what effect the removal of the udder had upon the agglutination titre, and whether the removal of the udder eliminated the focal infection.

Table I will indicate the dates and the agglutination end points.

TABLE I
AGGLUTINATION TITRES (Cow No. 132)

Date	Remarks	Agglutination end point	Days after removal of udder
July 24, 1928		1 : 10	
Oct. 2, 1928		1 : 10	
Nov. 3, 1928		1 : 10	
Dec. 10, 1928		1 : 100	
Feb. 4, 1929		1 : 400	
Apr. 24, 1929		1 : 600	
Apr. 29, 1929	Udder removed		
May 8, 1929		1 : 600	9 days
May 14, 1929	Aborted		15 days
May 15, 1929		1 : 600	16 days
May 21, 1929		1 : 400	22 days
June 10, 1929		1 : 400	42 days
June 26, 1929		1 : 400	58 days
July 8, 1929		1 : 400	70 days
July 29, 1929		1 : 200	91 days
Aug. 6, 1929		1 : 100	99 days
Aug. 14, 1929		1 : 100	107 days
Sept. 17, 1929		1 : 50	141 days
Oct. 23, 1929		1 : 50	177 days
Dec. 11, 1929		1 : 50	226 days
Dec. 26, 1929		1 : 25	241 days
Jan. 21, 1930		1 : 25	267 days
Mar. 18, 1930		1 : 25	323 days

Cow No. 227

This was a four-year-old animal that had aborted 10 months before, but had not been bred subsequently. She carried an unusually high agglutination titre (approximately 1-25,000) for nearly a year. Inoculation of guinea pigs

from each quarter together with plants on suitable media demonstrated the presence of *Br. melitensis (abortus)* in the four quarters of the udder.

After being starved for 24 hr. on June 6, 1929, the animal was placed under general anaesthesia, and the udder surgically removed. An examination of the organ and the supramammary glands did not show any macroscopic evidence of lesions. Each of these tissues was inoculated into guinea pigs. These became infected, and from their spleens *Br. melitensis (abortus)* was isolated, thus proving the presence of the organism in the udder and supramammary lymph glands.

Table II contains the dates on which the blood samples were drawn, and the end point of the agglutination tests.

TABLE II
AGGLUTINATION TITRES (COW No. 227)

Date	Remarks	Agglutination end point	Days after removal of udder
June 6, 1929	Udder removed	1 : 28000	
June 14, 1929		1 : 26000	8 days
June 27, 1929		1 : 2560	21 days
July 3, 1929		1 : 1200	27 days
July 14, 1929		1 : 800	38 days
July 29, 1929		1 : 400	53 days
Aug. 7, 1929		1 : 200	62 days
Aug. 27, 1929		1 : 100	82 days
Sept. 24, 1929		1 : 100	110 days
Nov. 8, 1929		1 : 100	155 days
Jan. 31, 1930		1 : 100	229 days
Mar. 19, 1930		1 : 100	286 days

Discussion

It is perhaps unwise to draw a conclusion from the above recorded experiments, although it seems clear that the removal of the udder was in each case followed by a reduction in agglutination titre.

In the case of animal No. 132 the gradual disappearance of agglutinins, which finally fell to within the negative range, would seem to indicate the removal of the focus of infection.

In the case of cow No. 227 the results are more difficult to interpret. The remarkably rapid fall of the agglutination titre after the removal of the udder is significant. It must be borne in mind, however, that this animal has not yet reacted negatively. It will be necessary for a longer period of time to elapse before a definite conclusion can be drawn.

References

- SCHROEDER, E. C. Bur. Anim. Indus. Circular 198, or Exp. Sta. Record 27:281. 1912.
- SCHROEDER, E. C. and COTTON, W. E. J. Agr. Research 9:9-16. 1917.
- SMITH, T. and FABYAN, M. Centr. Bakt. I. Abt. Orig. 61: No. 7. 549-555. 1912.

NOTE ON TUBERCLE BACILLI OF AVIAN ORIGIN HARBORED IN THE UDDER OF A COW¹

BY CHAS. A. MITCHELL² AND R. C. DUTHIE³

Abstract

Tubercle bacillus, isolated from an avian source, the common crow, remained alive in the udder tissue of a cow 210 days after intravenous inoculation without producing demonstrable macroscopic lesion; reinoculated from the udder tissues into laboratory animals it proved virulent, and caused progressive lesions in chickens and rabbits but not in guinea pigs.

Introduction

In February 1928 in the course of a study of tuberculous infections occurring naturally in crows (*Corvus brachyrhynchos brachyrhynchos*) the authors isolated two strains of tubercle bacilli (1). One of the strains was used in an experiment made with the object of determining the fate of these tubercle bacilli in the body of a bovine animal.

Experimental

Cow No. 227, Holstein, four years old, out of a supervised herd, and always a non-reactor to repeated tuberculin tests, but a carrier of *Br. melitensis* (*abortus*).

Oct. 24, 1928. Intracutaneous tests with avian and bovine tuberculins: negative.

Oct. 30, 1928. Intravenous inoculation with 200 mg. of tubercle bacilli (Crow Strain I).

Nov. 8, 1928. Reinoculation, intravenous, with 500 mg. of tubercle bacilli (Crow Strain I).

Mar. 13, 1929. Tuberculin tests with avian and bovine tuberculins: positive. The reaction to the avian was about double that to the bovine tuberculin.

June 6, 1929. Udder amputation carried out under general anaesthesia, and in connection with experiments with *Br. melitensis* (*abortus*) infection.

The entire udder was sliced into very thin sections, and a careful examination did not reveal the presence of any macroscopic lesion. A small portion of apparently normal udder tissue was ground and injected intraperitoneally into a chicken 'LB 251' and several guinea pigs.

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TABLE I
RESULTS OF EXPERIMENTS

Passage	Animal		Inoculum	Route	Reactions to tuberculin			Death in days	Result
	No.	Species			Days after inoculation	Avian	Bovine		
1st	227	Cow	Tubercle bacilli Culture crow (Strain 1)	Intravenous	134 days	Positive	Positive		Udder removed 210 days after inoculation — no ma- croscopic evidence of tuber- culosis.
2nd	L.B. 251 184 185 186	Chicken G. pig " " "	Udder cow 227 " " " "	Intraperitoneal " " " "	95 days — — —	Positive — — —	Positive — — —	K 106 days K 45 days K 45 days K 45 days	Progressive tuberculosis No evidence of tuberculosis No evidence of tuberculosis No evidence of tuberculosis
3rd	L.B. 254 250 251	Chicken Rabbit G. pig	Lesion chicken 251 " " " "	Intraperitoneal " " " "	— — 116 days	— — Positive	— — Negative	D 67 days D 120 days (living) 179 days	Progressive tuberculosis Progressive tuberculosis — — — —
4th	279 320 349	Chicken Rabbit G. pig	Lesion chicken 254 " " " "	Intraperitoneal " " " "	52 days — 46 days	Positive — Positive	Positive — Positive	(living) 109 days 109 days 109 days	

The guinea pigs were destroyed six weeks later in connection with the *Br. melitensis* (*abortus*) experiment. No visible lesions of tuberculosis were found.

The chicken was out of the healthy flock, in which all birds are hatched and raised until taken for experimental purposes, under continuous strict isolation, and are periodically tested with tuberculin. No reactor has ever been found among them.

Chicken LB 251 was challenged June 6, 1929 with avian and bovine tuberculin, and gave negative reactions. Chicken LB 251 was tested with avian and bovine tuberculins 95 days after inoculation, a thick 4X reaction being obtained from avian tuberculin and a 2X reaction from bovine tuberculin. This bird was destroyed for necropsy 106 days after inoculation. Necropsy findings: large conglomerate tuberculous mass at the site of inoculation; many nodular and miliary tubercles involving pancreas and mesentery; few small tubercles in the lung; acid-fast micro-organisms numerous in lesions.

A guinea pig and a chicken, LB-254, both tested with avian and bovine tuberculin and giving negative reactions, and also a rabbit were inoculated with tuberculous material from this bird. The chicken LB 254 died in 67 days; one-half of the left and two-thirds of the right lung were transformed into a solid, caseous mass, teeming with acid-fast micro-organisms; there were few pin point lesions in the liver and spleen, few nodular tubercles on the wall of the intestine, few scattered tubercles on the peritoneum. Acid-fast micro-organisms were relatively numerous in smears from bone marrow.

Rabbit No. 250 died 120 days after inoculation with extensive generalized tuberculosis. Guinea pig No. 251 is still living, and it reacts to avian tuberculin only.

A chicken, a rabbit and a guinea pig have been injected with tuberculous material from chicken LB 254. The chicken and guinea pig react to both tuberculins but give much stronger and better defined reactions to avian tuberculin.

Reference

1. MITCHELL, C. A. and DUTHIE, R. C. Am. Rev. Tuberculosis. 19:134-139. 1929.

SINKAGE STUDIES I. THE MODE OF PENETRATION OF WATER INTO LOGS: PRELIMINARY FIELD EXPERIMENTS¹

BY GEORGE W. SCARTH² AND EDWIN C. JAHN³

Abstract

The distribution of water in logs, floated in a lake, was determined and found similar to that in living trees. The trees examined belonged to the following species: jack pine, spruce, poplar and balsam, in which there is a relatively dry heartwood becoming wetter in the order named, the sapwood being wet all around, and birch in which the heartwood is equally as wet as the sapwood.

The rate of radial penetration of water into the logs seems to increase in the order, birch, jack pine, spruce, balsam, poplar. Penetration takes place very slowly, even into sapwood. The advantage of a large proportion of relatively dry heartwood depends more on the initial buoyancy it confers, than on the greater resistance to penetration it may possess. Narrow outer rays and density of the wood diminish the rate of penetration in the samples studied. In air-dry logs, penetration of free water is also very slow; saturation of the cell walls precedes it at a more rapid rate. The gas in floated logs is enveloped by water and can escape only in solution. There is evidence that more gas may be liberated by fermentation of storage material in the parenchyma cells. Whether escape of gas or penetration of water is the leading factor in determining rate of sinkage is undecided at present.

Introduction

The experiments described in this and subsequent papers are directed primarily towards a solution of the practical problem of minimizing the sinkage of pulpwood during flotation. Incidentally, they contribute to our knowledge of the physiology of trees. The species of tree studied are those mainly used for pulp production in Eastern Canada, namely, white and black spruce, jack pine, balsam, paper birch and poplar (*aspen*). Serious loss among softwoods is practically confined to the top logs of a tree, but with hardwoods all parts of the bole float so badly that this group is rarely utilized except where a short drive, or none, is required. Since any device, by which the floatability of hardwoods could be economically improved, would open up large fresh resources of supply, special attention is devoted in later work to the study of these woods, particularly birch.

The problem is being attacked in various quarters from the practical standpoint. It is here approached by way of investigating the mechanism of processes taking place in the log. This is much more complex than might at first appear.

Three phases are present: wood, water and gas. Since the density of the first phase is about 1.5, a volume of gas equal to half the volume of solid matter must be included to enable a log to float at all. The length of time any log will

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float depends on two things, not necessarily related: first, its initial buoyancy, and second, the rate at which it loses buoyancy when put in the water. The former depends merely on the *proportions* of the three phases present, the latter on their relative *distribution*, as well as on other factors. The amount and distribution, therefore, of wood, water and gas in trees and logs is the subject of the present study. Distribution, in a special sense, involves structure of wood. It will simplify the subsequent discussion if at the outset these features of wood structure be mentioned, which seem to have most influence on its permeability, both to water and gas.

WOOD STRUCTURE AND PENETRATION OF WATER

Regarding the mode of entry into a log, a distinction may be made between capillary flow and permeation through cell walls. The opportunities which exist for the former are largely determined by the presence of channels adapted to the normal flow of sap, namely, open vessels and functioning bordered pits. In addition, resin canals have to be considered in the case of conifers. In this connection, reference may be made to studies of the relation between structure of wood and permeability by Bailey (1), Teesdale and Maclean (14), Gerry, Stamm (13), Johnston (8) and one of the present writers (11). Especial importance is to be attached to the existence of *tyloses* of the vessels in the case of hardwoods, and to pit closure in the case of conifers as the principal factors which tend to differentiate between heartwood and sapwood as regards permeability to the flow of liquid or gas. Sapwood in spruce and pine is usually enormously (100 to 100,000 times) more permeable to longitudinal penetration of water, mercury, etc., under pressure, than is heartwood, and microscopic examination shows that this is due to aspiration of the pit membranes in the latter*. The permeability of balsam heartwood is considerably greater (12) than in the case of the above, and a study of radial sections indicates that in about 10% of the pits in the heartwood of balsam the torus is not pressed to one side of the pit cavity*. In the heartwood of spruce and white pine it is only in the latest summer wood that the pits, here greatly reduced, fail to close. In jack pine the summer wood forms a rather broad, well-defined zone of thick-walled elements in which the pits are reduced and ineffective as regards closure. However, they are also few in number. Except in these zones of summer wood, which are very narrow in spruce and balsam, the only channel through which water can pass in coniferous heartwood is the ultramicroscopic pores in the walls of the tracheids, and the passage is correspondingly slow. The superior floating powers of softwood logs with a high proportion of heartwood is familiar to loggers, and is proved by experiment. One of the questions to be considered is how far this is due to the greater resistance of heartwood to penetration, and how far to other properties which the heartwood may possess.

* The membrane (except the torus) of bordered pits is minutely perforated, so that not only water, but small particles and even mercury can easily pass through as long as the membrane stretches free across the chambers. In conifers as a rule the change of heartwood to sapwood is attended by a sealing of the membrane to one side of the pit cavity, so that the torus covers the opening, and the permeability of the pits is lost. No such change takes place in very reduced pits of conifers and probably not in hardwoods (1, 12).

The foregoing remarks on permeability apply mainly to longitudinal penetration, but the end surface of a log of ordinary dimensions constitutes only a small fraction of its total area, and end penetration is not found to be a large fraction of the whole. In the radial direction, along which most of the water enters, open communication is scanty. In conifers, only the ray tracheids and such radial resin ducts as are not plugged, provide channels through which water can flow. In hardwoods, tangentially situated bordered pits are not lacking in the longitudinal elements as they are in conifers, but in the fibres and fibre tracheids they are few and reduced. Does the radial penetration of water take place mainly by capillary flow through microscopic pores or by infiltration through the walls? Does it principally follow the rays or cross the fibre? The relation of permeability to specific structure, to rate of growth and to density will be better understood if the route which the water mainly follows be known.

WOOD STRUCTURE AND ESCAPE OF GAS

Pari passu with the increase in volume of the aqueous phase in a log the gaseous phase must diminish. In so far as the gas is free to escape en masse, the resistance which it experiences in passing through small openings is negligible compared with the resistance to passage of water, and the latter sets the pace. But one of the critical questions to be considered is how far the gas in a log is free to escape in this way, or how far it must escape by solution in the water and diffusion to the exterior. In so far as the latter is its mode of escape, the density of the wood, especially the outer wood, is the most important structural feature. This varies with the species and with growth conditions. In conifers slow growth generally produces narrow rings with a high proportion of thick-walled summer tracheids. In birch, however, density decreases only slightly with rate of growth. The principal difference between fast and slow-grown birch wood, such as might affect permeability either to gas or water, would appear to be the shorter ray cells in the latter.

Many other factors besides wood structure influence the rate at which imprisoned gases can escape by solution, but a discussion of these is reserved until experiments on the relation of water and gas in floating logs have been described.

Literature

A survey of the published data on the sinkage of logs reveals that very little work has been done on the problem, though a good deal is now in progress. The most important recent investigation is that of Boberg and Juhlin-Dannfelt (2) carried out in Sweden on pine logs. These authors made the important discovery that there is seasonal fluctuation, the buoyancy being influenced, apparently, by fermentation in the logs. During the hot summer months there is but little loss of floating power in the logs, and in many cases even slight gains. This fact raises important theoretical considerations.

Kinnman (9), also in Sweden, has published some data on the floatability of timber. He has investigated the relation of buoyancy to such factors as proportion of spring to summer wood, fast growth versus slow growth, and mainly to the proportion of heartwood in the log.

The more important considerations of the work of Boberg and Juhlin-Dannfelt (2) as well as that of Kinnman (9) have been discussed in a theoretical study of the sinkage problem by the senior author (11).

No study has been made, apparently, of water distribution in floated logs, but W. G. Craib (3) has investigated the regional distribution of moisture in several species of trees during different seasons of the year. He found very appreciable differences in both the total percentage of moisture and its distribution. In *Acer*, during the winter and spring, water accumulates in the heartwood, reaching a maximum in March. As the leaves come out, the water content decreases greatly, reaching a minimum in August, when there is a large, comparatively dry heartwood area, surrounded by a narrow wet outer zone of sapwood.

However, in the case of such resinous conifers as *Chamaecyparis*, *Larix*, *Pinus* and *Cedrus*, no moisture storage was found in the heartwood. In *Chamaecyparis* (cut in October) a very high moisture percentage was found in the sapwood, namely 240-250% at the base, 250-260% midway and 200% at the top of the bole. In the heartwood the moisture content averaged between 40 and 50%. Moisture distribution in resinous conifers thus approaches the condition reached by *Acer* in August. These results apply to the climatic conditions of Scotland.

Earlier determinations by T. A. Hartig (6) and Geleznow (4) had shown that in Germany, the total water in all kinds of trees is least in summer, and greatest in winter for conifers, and in spring for hardwoods. R. Hartig (5) however, disputed this. He found that day and night variations were important.

Methods

The floated logs studied in this investigation were all selected from the Sinkage Study booms located on the forestry limits of the Wayagamack Pulp and Paper Company Limited.

The logs were floated May 8, 1928, (dead cut logs May 10) and since the field work was carried out in August, the logs examined had floated about 12 to 15 weeks.

Three sound, living trees—a balsam, jack pine and a black spruce—were felled at Lac Gagnon during August, and a regional distribution of their moisture content determined at three places in the bole, namely, near the butt, about half way up, and near the top, just above or near the first branches.

Investigations of the moisture content and distribution, the relative proportion of gas and water in the various tissues, were carried out by two methods (a) gravimetric determination of moisture and (b) microscopic examination of the tissues.

a. Gravimetric determinations

One or two transverse discs about 2.5 to 4 cm. thick were cut at selected positions in the log or tree, and a strip 2 to 2.5 cm. wide was cut across the middle of the disc. This was then cut, parallel to the annual rings, into small blocks at measured distances. The width of these blocks ranged from about 0.5 cm. to 2 cm., the smaller blocks being cut in the outer sapwood. These small blocks were numbered and weighed immediately after cutting to prevent loss of moisture by evaporation. Later they were dried in an oven at 100-105° C. to constant weight (48 hr.) and before weighing again, allowed to cool in a desiccator over anhydrous CaCl_2 . The volume of each block was determined by immersion in mercury contained in a graduated cylinder.

From these measurements were calculated the weight percentage and also the volume percentage of water with reference to that of the dry wood blocks. This latter value eliminates the density factor in the wood. In this manner the distribution of water by weight and by volume was calculated across the diameter of the log, and its variation determined.

b. Microscopic examination

The microscopic examination included observations at various distances across the diameter of the log in the same discs from which the above blocks were cut.

The sections, principally radial, were cut by razor immediately after weighing the blocks, and at some little distance within the wood.

It was found that the mounting medium caused no—or very little—alteration in the distribution of gas and water inside the sections. No movement or displacement of the air bubbles took place, even when the bubbles were exposed by the cut end of a tracheid.

Results

REGIONAL DISTRIBUTION OF WATER IN LIVING TREES

Jack pine

Examination of Fig. 1 and Table I shows that the distribution of water in living jack pine in August presents but little variation between the top, middle and butt sections of the bole. There is a slight increase in moisture in sapwood as the bole is ascended, but the heartwood is fairly uniform throughout. The average per cent weight water in the outer sapwood is 141%, whereas the percentage moisture in the heartwood is about 33%, which is barely above

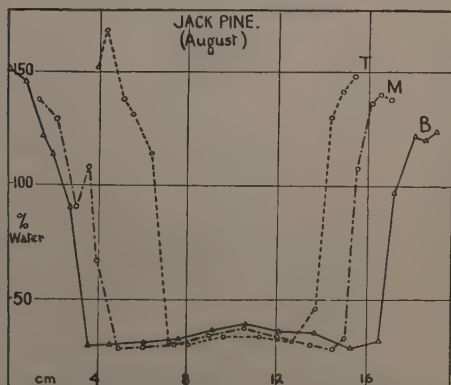


FIG. 1. The distribution of water in living jack pine in August.

that required for saturation of the cell walls (1), showing that there is no appreciable amount of free water in the heartwood. The sharp delimitation between heartwood and sapwood as regards moisture is notable.

TABLE I
DISTRIBUTION OF WATER IN JACK PINE

Position		Per cent of dry weight and dry volume					
		Sapwood			Heartwood		
		Outer	Central	Near H.W.	Outer	Intermediate	Centre
Top	Wt. %	153	135	120	39	32	34
	Vol. %	69	62	53	18	14	15
Middle	Wt. %	136	119	97	30	31	37
	Vol. %	67	53	48	13	13	13.4
Butt	Wt. %	134	119	93	29	33	38
	Vol. %	69	60	46	16	17	15
Av.	Wt. %	141	124	103	33	32	36
	Vol. %	69	58	49	16	14.6	14.4

NOTE: Description of tree: Cut August 5, 1928; sound; (diameter breast high), 19 cm.; age 84 yr.; height 16.75 metres (55 ft.); width last 10 annual rings, 0.6 cm. (0.25 in.).

Diameter of discs used and width of sapwood were as follows:

	Diameters			Width of sapwood	
Butt disc	19	by 17	cm.	2.8	and 2.4 cm.
Middle disc	15.4	" 13.7	"	2.5	" 1.9 "
Top disc	12	" 11.2	"	2.8	" 1.8 "

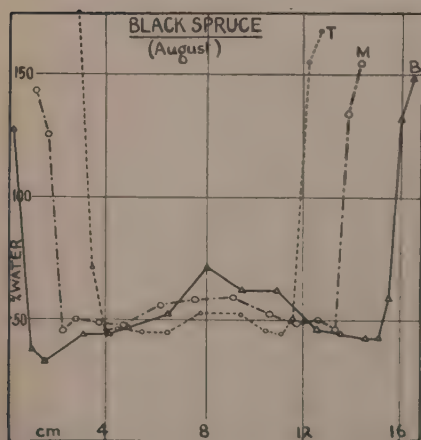


FIG. 2. The distribution of water in living black spruce in August.

Black Spruce

Examination of Fig. 2 and Table II shows that there is a little free water in the heartwood of black spruce in August, the average weight per cent being 49. The percentage of water in the sapwood increases slightly from the butt to the top of the bole, and conversely the amount of water in the central portion of the heartwood decreases slightly from the butt to the top. However, the total average percentage of water in the heartwood is nearly constant throughout the bole.

TABLE II
DISTRIBUTION OF WATER IN BLACK SPRUCE

Position			Sapwood		Heartwood	
			Outer	Total	Central Region	Total
Top	{	Wt. %	42	169	51	48
		Vol. %	21	170	27	24
Middle	{	Wt. %	46	140	58	51
		Vol. %	23	68	30	24
Butt	{	Wt. %	48	134	65	49
		Vol. %	23	67	35	25
Av.	{	Wt. %	45	154	58	49
		Vol. %	23	68	31	24

NOTE: Description of tree: Cut August 7, 1928; sound; diameter breast high, 16.7 cm.; age 140 yr.; height 16.75 metres (55 ft.); width last 10 annual rings, 0.38 cm. (0.15 in.).

Diameter of discs used and width of sapwood:

Diameter

Butt disc 16.4 by 15.3 cm.
 Middle disc 14 cm.
 Top disc 10.3 cm.

Width of sapwood

1 cm.
 1 cm.
 0.7 and 1 cm.

Balsam

Examination of Fig. 3 and Table III shows, as in the case of black spruce and jack pine, that there is comparatively little difference in balsam between the curves for top, middle and butt sections of the bole. In the outermost sapwood there is an appreciable increase in water content from butt to top.

However, both in sapwood and heartwood there is a large increase in water over the figures for black spruce and jack pine. For sapwood, the average percentage weight of water is 239% and for heartwood 109%. Thus, there is a large amount of free water throughout the living tree in August, both in the sapwood and heartwood.

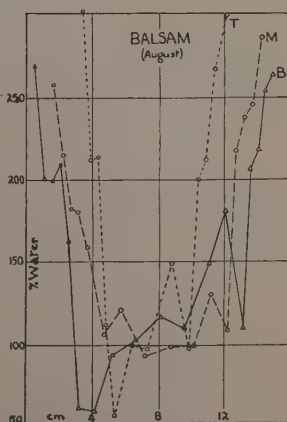


FIG. 3. The distribution of water in living balsam in August.

TABLE III
DISTRIBUTION OF WATER IN BALSAM

Position		Sapwood			Heartwood		
		Outer	Central	Near H.W.	Outer	Intermediate	Centre
Top	Wt. %	300	227	180	87	111	122
	Vol. %	96	71	56	30	37	40
Middle	Wt. %	277	212	193	106	117	96
	Vol. %	91	74	72	41	40	34
Butt	Wt. %	246	208	193	92	126	127
	Vol. %	77	72	68	32	42	48
Av.	Wt. %	274	216	189	95	118	115
	Vol. %	88	73	65	34	39	40

NOTE: Description of tree: Cut August 7, 1928; sound; diameter breast high, 16.5 cm.; age 30 yr.; height 9.15 metres (30 ft.); width last 10 annual rings, 3 cm. (1.2 in.).

Diameter of discs used and width of sapwood:

	Diameter	Width of sapwood
Butt disc	15 by 14 cm.	2.5 and 2 cm.
Middle disc	13 " 12 "	2.5 " 2 "
Top disc	9 " 8.7 "	2 cm.

Comparison of moisture distribution in living trees cut in August

Comparison of the curves representing the water content of live jack pine, black spruce and balsam in August shows them to be of the same general type, that is, a high percentage of water in the sapwood, especially in the outer part, and a comparatively low percentage throughout the heartwood.

The figures in Tables I, II and III show that jack pine contains more water than black spruce and the latter more than balsam. The average weight and volume for the total sapwood and total heartwood are as follows:—

TABLE IV
AVERAGED ANALYTICAL RESULTS

Species	Sapwood		Heartwood	
	Weight %	Volume %	Weight %	Volume %
Jack pine	124	55	33	15
Black spruce	154	68	49	26
Balsam	239	76	109	37

The water content of living balsam being higher than that of jack pine or spruce gives it an initial disadvantage in floating ability.

The results suggest that the poor floating capacity of the top logs of conifers is due mainly to the higher ratio of sapwood to heartwood; this involves a greater amount of water which gives them a relatively low margin of buoyancy from the outset. Further the fact that there is a slightly higher percentage of water in the respective regions in top logs (cut in August at least) is an additional factor in their lesser buoyancy. Seasonal variations in the water content of trees will be given in a later paper.

PENETRATION INTO FLOATED DEAD CUT (AIR-DRY) LOGS

Fig. 4 represents the distribution of water across the diameter of three dead cut logs (two spruce and one balsam) which had been floated about 15 weeks.

The moisture is given in weight percentage in order to determine whether the cell walls only are saturated, or whether there is free water present. Values below 25-30% represent water of imbibition, whereas higher values indicate that free water is present in the cavities as well. In the case of the spruce, the side floating upwards has even its cell walls dried out to a considerable extent. Penetration of free water on the lower side extends for only a very short distance. The range where the steep portion of the curve begins to flatten out is the limit of penetration of free water. The cells over a distance of 1-2 mm. are completely filled and for only 1.5-2 cm. is there water in the cell cavities; beyond this range, there is only air, and differentiation lies in the quantity of water absorbed in the cell walls. The saturated condition of the cell walls extends far beyond the penetration of free water. This indicates that the cell walls imbibe water much faster than the spaces become occupied by capillary infiltration, the latter being a very slow process.

The original distribution of moisture in the dead cut logs, cut in February, is unknown. It may have been uniform throughout, or it may have risen towards the centre, and thus be represented by the left-hand half of the curve.

The curve for balsam is of the same general type as for the dry floated spruce, except that penetration of free water extends much further in, and is less uniformly distributed.

In order to determine whether these curves are typical for logs which are air-dry throughout when floated, additional experiments were carried out in the laboratory. Three short logs, or bolts (two spruce and one balsam) 18

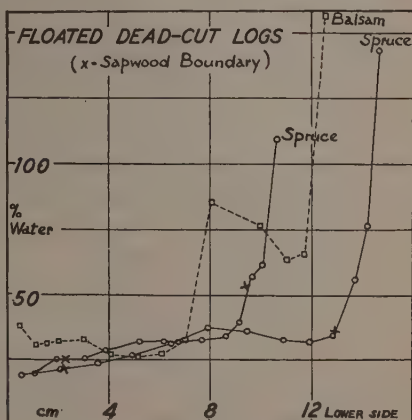


FIG. 4. The distribution of water across the diameter of dead-cut logs.

to 23 cm. (7 to 9 in.) long and about 13 cm (5 in.) in diameter, which had been kept in a warm dry room for seven months, and were uniformly air-dry throughout, were painted on the ends with asphalt paint to reduce end penetration. They were then floated in a tank for 10 weeks, after which time the moisture distribution was determined by examining a disc cut from the centre of each log.

The results of these experiments confirm the conclusions drawn above for floated dead cut logs. Moisture distribution curves are of the same type as those representing penetration into the dead cut logs. Penetration of free water extends for only a comparatively short distance into the wood, whereas saturation of the cell walls goes entirely across the bolt.

DISTRIBUTION AND PENETRATION OF WATER IN FLOATED LIVE CUT LOGS

Most of the work carried out in this investigation was concentrated on the study of some of the logs in the sinkage boom at Lac Gagnon. These logs were cut in February 1928 and placed in the water by May 8, 1928, when the ice went out. The boom was located in a quiet bay in shallow water. The temperature of the water during the time of floating varied as follows: May 17, 57° F.; June 5, 58° F.; June 19, 62° F.; July 18, 68° F.; August 16, 69° F. (Forestry Department Records).

The following species were examined:

	<i>No. of logs</i>	<i>No. of samples investigated</i>
Balsam	9	20
Jack pine	4	8
Black spruce	2	4
White spruce	3	5
Birch	3	5
Poplar	1	1

In most cases two discs were cut from each log, near the opposite ends of the log. A distance of 13 cm (5 in.) from the end was usually found to be beyond the range of end penetration, but nearly all samples were selected at least 20 to 38 cm. (8 to 15 in.) from the end of the log.

In all cases with floated logs the sample strip cut for gravimetric determinations was cut, perpendicular to the water line of the floating log. In this way the distribution of water was determined, from the upper side of the log (above water) to the bottom side (below water). In all the Tables and graphs, unless otherwise stated, left to right represents top to bottom of the logs.

The average water distribution in the different species is shown in Table V and plotted in Fig. 5 and 6.

TABLE V
AVERAGE DISTRIBUTION OF WATER IN VARIOUS SPECIES

Species	Weight per cent of water in floated logs													
	Upper sapwood				Heartwood						Lower sapwood			
	Width, in cm.	Outer	Centre	Near heartwood	Diameter, in cm.	Outer	Inter-mediate	Centre	Inter-mediate	Outer	Width, in cm.	Near heartwood	Centre	Outer
Jack Pine	2.34	138	131	101	9.0	45	36	38	34	48	2.82	104	132	135
Balsam	1.7	215	201	170	9.3	111	113	109	118	130	1.8	198	218	218
Black spruce	1.95	151	144	118	9.7	62	43	52	42	76	2.12	150	161	159
White spruce	1.78	158	152	119	9.4	63	47	50	46	57	2.06	121	146	157
Birch	6.0	89	79	87	4.04	105	105	102	99	97	6.22	82	85	97
Poplar	4.5	187	179	167	9.0	91	58	65	56	83	4.7	150	190	192

The curves for conifers show a striking resemblance to those for the fresh cut trees already given and later work has shown that the same resemblance holds also for hardwoods. All species, except birch, are much wetter in the sapwood than in the heartwood.

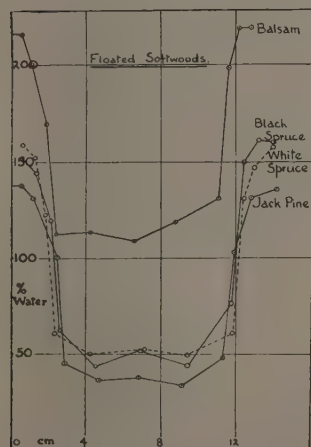


FIG. 5. The distribution of water in floated softwoods.

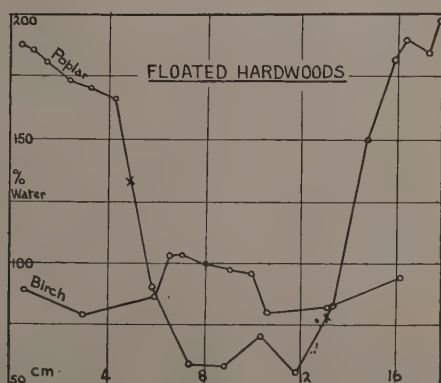


FIG. 6. The distribution of water in floated hardwoods.

It is unfortunate that it is not known precisely how much of the water is influx. Nevertheless, some tentative comparisons of penetrations in the different species can be made by comparison between floated and fresh cut logs. Since the floated logs were cut in February, some figures for the condition of the respective trees at the date (Table VI) are borrowed from later work. There

would be little drying so long as the logs were frozen and since they were floated on May 9—immediately the ice was gone—they had little time to alter profoundly in the interval of thaw. The difference between figures for floated logs and those for the same species in the growing tree gives some indication, therefore, of the relative amounts of water taken up. In conjunction with this, however, it should be noted, as later studies have shown, that birch (on account of its density and the central storage of water) dries more slowly than the others.

TABLE VI
COMPARISON OF THE DISTRIBUTION OF WATER IN FRESH CUT
LOGS AND THE LOWER SIDE OF FLOATED LOGS

		Water in per cent of dry weight and volume			
Region of log	Fresh cut February	Floated May to August	Difference		Radial thickness
			% dry wt.	% dry vol.	
BIRCH					
Outside	77	97	+20	+30	} 6.2 cm.
Next	85	85	0		
Next	85	82	- 3		} 2.0 cm.*
Next	90	97	+ 7		
Centre	97	100	+ 3		
POPLAR					
Outer Sapwood	138	191	+53	} +120	} 4.7 cm.
Inner Sapwood	96	150	+54		
Outer Heartwood	69	83	+14		} 4.5 cm.*
Inner Heartwood	67	60	- 7		
JACK PINE					
Outer Sapwood	155	134	-21	} +30	} 2.8 cm.
Inner Sapwood	72	104	+32		
Outer Heartwood	35	48	+13		} 4.5 cm.
Inner Heartwood	33	36	+ 3		
SPRUCE					
Outer Sapwood	155	166	+11	} +40	} 2.1 cm.
Inner Sapwood	108	135	+27		
Outer Heartwood	41	66	+25		} 4.6 cm.
Inner Heartwood	44	47	- 3		
BALSAM					
Outer Sapwood	193	218	+25	} +100	} 1.9 cm.
Inner Sapwood	145	198	+53		
Outer Heartwood	128	130	+ 2		} 4.6 cm.
Inner Heartwood	128	113	-15		

* Half the diameter of the heartwood.

A strict comparison between the two sets of measurements is impossible since the spacing of the samples was not quite the same in both cases. Comparing the sapwoods, however, and allowing for differences of density of the respective species, the increase in water content in the floated logs as compared with February cut trees is, in round numbers, in cc. per 100 cc. of wood: 120 in poplar, 100 in balsam, 40 in spruce, 30 in jack pine and 30 in birch. The depth to which the increase extends appears to be least in birch. In most species there is a slight increase in the outer heartwood. Balsam should probably show more, as the heartwood moisture in the February cut trees is abnormally high. On the whole, penetration of heartwood is apparently a minor factor in loss of buoyancy during the first few months of flotation, so that, as Boberg and Juhlin-Dannfelt (2) have argued, with reference to the importance of a due proportion of heartwood, the relative impermeability of this region in most species is a less important factor than the reserve of buoyancy conferred by its initial low water content.

The effect of density of wood on penetration seems to be illustrated both as regards different species and different growth types within a species. The order of increasing density among the conifers is, generally, balsam < spruce < jack pine, and among the hardwoods, poplar < birch. Birch only, however, varies at all widely from the rest. In the individual species the rate of penetration seems to be governed largely by the width of the outer year rings, which is usually correlated with density. The distinction is most clearly shown in balsam (Fig. 7). Each curve represents an average of five samples taken from three logs. Table VII shows the correspondingly greater loss in buoyancy for logs with wide outer rings. The figures indicate in inches the rise above water level.

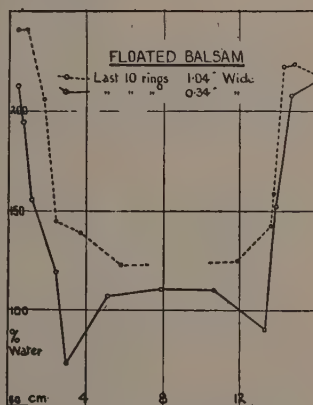


FIG. 7. *The distribution of water in floated balsam.*

TABLE VII

RELATION OF LOSS OF BUOYANCY TO OUTER RING WIDTH IN BALSAM

Outer 10 rings	Rise above water level, in inches		
	Initial rise (May 17)	Final (August 16)	Loss
Narrow, 0.35 in. (0.9 cm.). (S.W. 1.55 cm. H.W. 11.5 cm.)	1.65	0.95	0.7
Wide, 0.85 in. (2.2 cm.). (S.W. 1.9 cm. H.W. 9.5 cm.)	1.60	0.25	1.35

The same was seen in the case of jack pine. The slightly higher water content in black spruce than in white spruce is probably due also, in part at least, to the slight difference in outer ring widths (Fig. 5).

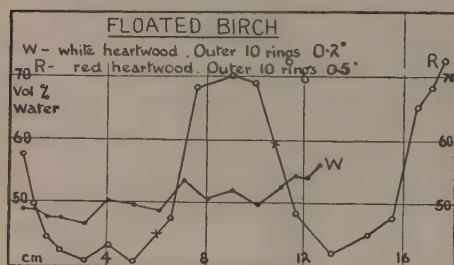


FIG. 8. *The distribution of water in floated birch, showing the effect of the density of the wood on penetration.*

Even birch, in which the density decreases but slightly with the width of the annual rings, shows less absorption in slow-grown wood. This is shown in Fig. 8 together with the effect of red heart on the original moisture content. This suggests that the radial dimensions of the ray cells, to a greater extent than wood density, is the regulative feature.

All these comparisons are made with reservation on account of the small number of

samples examined, but they appear to be in agreement with statistical studies on a larger scale. Attention is here drawn to them merely because they may throw some light on the mode of penetration of water.

Before discussing this subject, it is necessary to record some microscopic observations.

MICROSCOPIC OBSERVATION OF THE WATER-GAS RELATION IN FLOATED LOGS

The principal fact which can be readily observed is that the gas occurs inside the cells as large or small bubbles enveloped by water. This is true of the upper as well as the lower side of the floated logs and of the heartwood largely as well as the sapwood. Towards the outside the regions best filled with water are the rays and late summer wood except in jack pine, where, though the rays are full of water, the summer wood is almost without any. The distribution suggests that water entering the logs principally through the rays, the radial path of least resistance, is drawn most forcibly along the narrow summer tracheids by capillarity; there is an exception where practically no pits are present to admit the water, as is the case in jack pine. In the inner sapwood, and in the heartwood, there is an increasing amount of air in the rays. In the heartwood of birch the vessels have little air, and the tracheids surrounding them, almost none. In the heartwood of poplar the vessels contain rather more air than in birch while the fibre tracheids are almost filled with air. But these conditions are probably original rather than induced by penetration.

Another point of interest is the occurrence of gas bubbles in the storage cells of the rays and even of the outer sapwood, at least in many specimens of spruce and balsam. All the floated balsam, spruce and birch were covered under water by a bacterial slime full of bubbles, and the above appearance

suggests fermentation inside the log, as deduced by Boberg and Juhlin-Dannfelt (2). Jack pine, which had no slime, had no bubbles in its sapwood rays. Its highly resinous character may perhaps have some antiseptic action. It is also significant that little signs of fermentation appear in the ray cells of dead cut logs. No doubt the stored foodstuffs had been destroyed or lost during the time the timber stood dead.

Discussion

The most striking fact emerging from the gravimetric study of water distribution in floated logs is that the water content is almost as high on the upper as on the lower side. It is unlikely that all the water in the upper sapwood was present initially, for two reasons: first, because the percentage rises steeply toward the surface—a condition which is soon lost in seasoning—and second, because it is higher than the probable content at time of cutting as given in Table V. The bark also was saturated on the upper surface, so that it is probable that the logs, since they floated low, were frequently washed over by waves. These logs were protected by a boom. Under normal driving conditions there is even less chance for logs to become dry on one side. On the other hand the air-dry logs floated high and remained dry above under the conditions of the experiment.

The heartwood of most species contains, as shown above, a large body of gas. This gas is enclosed in cells with water saturated walls, and the whole is enveloped by a more or less water-logged sapwood. It is very unlikely that the narrow intercellular spaces between the ray cells remain air filled. There is, therefore, no possibility of displacement of the gas en masse—except under favorable conditions from the cut ends of vessels which have not undergone tylosis, as in birch.

In the sapwood there are pits, through the pores of which air can be forced under a pressure sufficient to overcome the surface tension. But here there is no high pressure nor any evidence, gravimetric or microscopic, that gas tends to be displaced toward the upper side of the log by hydrostatic pressure or capillary force. The only avenue of escape for the gas under these conditions is by solution in the water and diffusion to the exterior.

In logs which contain in their upper part only water imbibed by the cell walls, at least as free a passage of gas as in living trees should perhaps be expected. According to Macdougall, Overton and Smith, there is often an open gas system both vertical and radial in the trunks of transpiring trees. If this be the case, the extremely slow penetration of water into dry logs cannot be due to the opposing pressure of enclosed gas—as might well be the case in wet logs—but must be due to the frictional resistance of the wood to passage of water.

With the experiments described so far it is not possible to decide whether entry of water or escape of gas is the process which tends to lag behind, or

whether the relation may vary. The question is of practical importance, because upon it depend the methods which might be taken to reduce the rate of sinkage.

These preliminary experiments also point to the necessity of acquiring a greater knowledge of the content and distribution of water in trees at different seasons and the influence thereon of various modes of drying and of duration of drying, since these factors primarily determine the floating life of logs. Further work on all these problems will be described in subsequent papers.

Acknowledgment

The authors wish to express their indebtedness to the Wayagamack Pulp and Paper Company for the facilities generously extended them in the use of their logs and trees.

References

1. BAILEY, I. W. Contributions from Laboratory of Wood Technology, Harvard School of Forestry. No. 1: 1-7. 1913.
2. BOBERG, and JUHLIN-DANNEFELT. Sinkage Studies by Woodlands Section, Canadian Pulp and Paper Association, Montreal, 1928.
3. CRAIB, W. G. Royal Botanic Gardens, Edinburgh, Scotland. 11(51)p. 1. 1918; 12(59) p. 187. 1920; 14(66)p. 1. 1923.
4. GELEZNOW, N. Ann. Sc. Nat. Bot. 6(3):344-357. 1876.
5. HARTIG, R. Bot. Zeit. 41:250-255. 1883.
6. HARTIG, T. A. Bot. Zeit. 26:17-23. 1868.
7. HAWLEY, L. F. and WISE, L. E. The Chemistry of Wood. 1926.
8. JOHNSTON, H. W. and MAASS, O. Can. J. Research. In the press.
9. KINNMAN, G. Sar ur Sven. Skogsvards Foreningens Tidskrift. 1925.
10. MACDOUGAL, D. T., OVERTON, J. B., SMITH, G. M. Hydrostatic-pneumatic System of Certain Trees; Movements of Liquids and Gases. 1929.
11. SCARTH, G. W. The Sinkage of Logs—Its Cause and Prevention. Report pub. by Canadian Pulp and Paper Association, Woodlands Section, Montreal.
12. SCARTH, G. W. and SPIER, J. D. Trans. Roy. Soc. Can. Sect. 5:269-279. 1929.
13. STAMM, A. J. J. Phys. Chem. 33:398-414. 1929.
14. TEESDALE, C. H. and MACLEAN, J. D. Bull. U.S. Dept. Agr. No. 606: 1-36. April 1918.

SINKAGE STUDIES. II. THE SEASONAL DISTRIBUTION OF WATER AND GAS IN TREES¹

BY R. DARNLEY GIBBS²

Abstract

The distribution of water and gas in trees has been studied together with the seasonal changes which occur in distribution. The species studied were balsam, jack pine, birch and poplar. In freshly cut soft woods, with the possible exception of balsam, the water content is fairly uniform and very high in sapwood, but constantly low in the heartwood. The water content in birch was higher in the centre than near the outside. In poplar, the reverse condition was found. The heartwood in jack pine contained about 12% water, the sapwood 52%.

The heartwood contains more gas than sapwood and consequently the higher the heartwood content, the better the floating properties of the log. In jack pine heartwood contains 60% of gas and the outermost samples about 23%.

Wood and density values are not constant, but vary considerably. Even by allowing for the variation of density across a log, the errors in measurement are scarcely reduced. A useful determination involves the examination of standardized lots of logs, and the restriction of seasonal and other measurements to these lots.

Introduction

This paper deals with distribution of moisture and gas* in trees, and with the seasonal changes in distribution which occur in Eastern Canada.

The results obtained are such as to suggest that relatively little is known of the forces at work, a matter for surprise when reference is found in Nehemiah Grew (2) to facts of distributional and seasonal change:

"That is to say, those *Vessels* in the *Wood*, which in the beginning of "*Spring* do often times carry *Liquor*; when the *Tree* begins to thrive and "many new parts to be formed and fed, are filled only with *Air*; *sc.* a "*Vegetable Air*."

Since the time of Grew many authors have noted that there are seasonal changes in the flow of sap in trees and "the sap is up", "the sap is down" have become household phrases.

To make moisture determinations has been, as it were, to face a dilemma. The physiologist looks for all variations, however slight, in water content across the log, noting particularly the boundaries of heartwood and sapwood, and all local variations due to flaws, knots and other factors. The lumberman is less particular; the gross distribution is sufficient for him. Practical considerations have inclined the author to favor the lumberman, using more trees and taking fewer samples from each than the physiologist would wish. It is hoped to remedy this fault later.

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* The term gas is used in preference to "air" because the composition and pressure of the gas mixture in trees varies.

The Distribution of Wood, Gas and Water in Trees

A complete study of timber with reference to wood, gas and water, should show the relative proportions of these materials in all parts of the log. It should be possible from it to determine the relative amounts of water in the lumina and in the walls, the varying density of the wood and the gas content of the cells.

It is possible to obtain such data by carrying out a series of measurements as described below. Early investigations, as a preliminary to seasonal measurements, were along these lines. The following facts must be known before it is possible to make the appropriate calculations: (a) Fresh (wet) weight of sample, (b) Dry weight, (c) Wet volume (i.e., volume when fully swollen), (d) Dry volume, (e) Specific gravity of the actual wood material. From these the following equations are obtained:

1. Density = $\frac{\text{dry weight}}{\text{dry volume}}$
2. Swelling = $\frac{(\text{wet volume} - \text{dry volume}) \times 100}{\text{dry volume}}$
3. % Composition (based on wet volume)
 - a. Wood = $\frac{\text{dry weight} \times 100}{1.56 \times \text{wet volume}}$
 - b. Water = $\frac{(\text{wet weight} - \text{dry weight}) \times 100}{\text{wet volume}}$
 - c. Gas = $100 - (\text{wood} + \text{water})$
4. % Water (based on dry weight)

$$= \frac{(\text{wet weight} - \text{dry weight}) \times 100}{\text{dry weight}}$$

1. *Density.* By this is meant the weight per unit dry volume of the sample block.

2. *Swelling.* When dry wood imbibes water, it swells considerably, and the extent of the swelling varies greatly with the species. It is expressed here as percentage increase of the dry volume. The question of swelling, as such, was of no particular interest except in so far as measurements of wet and dry volumes were necessary for other calculations. Variation in swelling, however, affects calculations based on wet volume.

3. *Percentage composition of sample.* The composition has been expressed as percentage of the wet volume. The reason for this is that the fresh material was wet, i.e., fully swollen, and its measurement gave the wet volume. The minimum water content of fully swollen wood is about 30% of the dry weight, and the results of measurements usually greatly exceeded this. In the heart-wood of jack pine alone was the water content near this minimum value (Fig. 3).

a. Wood. The assumption has been made that the density of the woody material itself is 1.56. This figure is, at best, an approximation, but probably not far from the true value. Dunlop (4) found a variation of 1.50-1.75. More recent results of Stamm (4) suggest a figure nearer 1.475.

b. Water. The freshly cut blocks were weighed (wet weight), dried to constant weight at 100° C. and reweighed (dry weight). The loss in weight was taken as water content. Small amounts of volatile resins are lost during drying, but they are negligible when compared with the loss due to water.

c. Gas. The volume of gas is given as $(100 - [\text{vol. of wood} + \text{vol. of water}])$. This involves the assumption that compression taking place in the process of imbibition is negligible. It is well known that compression does occur, but it is certainly so slight as to affect the results but little.

4. *Percentage water (based on dry weight).* This is the usual method of expressing water content, and is given in order that comparison with other results may be made. There is, of course, a direct relationship between this figure and that based on wet volume. The latter involves volume and density measurements and is impracticable when large numbers of samples are to be handled, but assuming that the density and swelling in any one species are constant, the percentage of water based on dry weight can be translated into that based on wet volume by the relationship:

$$\text{percentage water (based on wet volume)} = \frac{\text{water (based on dry weight)} \times \text{density}}{\text{swollen volume}}$$

where the swollen volume is expressed as a fraction of the dry volume. A single example will suffice to illustrate this point:

The percentage water (based on dry weight) in a birch block was 75. Taking the density of birch as 0.6 and the wet (swollen) volume as 1.20 then:

$$\text{percentage water (wet volume)} = \frac{75 \times 0.6}{1.2} = 37.5$$

If the density and swelling are constant, then the ratio $\frac{\text{density}}{\text{swollen volume}}$ may be used as a conversion factor (in the example above, $\frac{0.6}{1.2} = 0.5$). Density and swelling are not constant, however, but the error involved, at least in the case of birch, is not large.

Methods

The method of sampling used was essentially that described in the first paper of this series (5). The blocks were treated and measured as follows:

1. Weight as cut = "wet weight".
2. Dried at 100° C., and reweighed = "dry weight".

3. Soaked in water until fully swollen and then measured in the volumeter (Fig. 1) = "wet volume".

4. Redried, greased to prevent water penetration, and remeasured in the volumeter = "dry volume".

Volume Measurement

Many methods for the measurement of volume have been described, and that given here differs only in detail from some of them. It is relatively simple, rapid and reasonably accurate and worked so well in practice (the following figures represent about 320 determinations) that it is described at some length.



FIG. 1.
*Apparatus
used in the
determination
of volume.*

The volumeter (Fig. 1) consists of a glass vessel with a very accurately ground stopper provided with inlet tube and funnel. The lower end of the vessel has a stopcock for emptying. The exact volume of this apparatus is known; a calibration mark being etched on the inlet tube. The block to be measured is placed in the vessel and the remaining space filled from a burette. By subtraction from the volume of the volumeter the volume of the block is given. A number of objections to this method may be raised, the most serious being: (a) the possibility of variation in volume of the apparatus due to difficulty of exact replacement of the stopper; (b) volume changes due to temperature fluctuation; (c) penetration of the liquid used into the block of wood; and (d) formation of air bubbles with consequent error.

A series of experiments showed that with a standardized technique and the following precautions the results were much more nearly accurate than has been supposed.

(a) The use of a minimum of grease on the stopper, careful grinding in and orientation, gave the following consecutive readings for volume: 92.04, 92.06, 92.04, 92.07, 92.06 ml.

(b) Avoiding temperature fluctuations by keeping the water used at exactly room temperature.

(c) Penetration of liquid into the block of wood was one of the most difficult problems. It was decided, after several trials, to saturate the blocks before measuring the wet volume, and to grease the dry blocks slightly* before making dry volume measurements.

(d) The use of grease increased the error due to air bubbles, but this was removed by careful manipulation and frequent cleaning of the apparatus.

The following consecutive readings for the volume of a single block are representative: 11.29, 11.33, 11.29, 11.31, 11.34 ml. The error involved is too small to affect the results seriously.

* This was done by rubbing with albolene.

Series of measurements involving the species used throughout these investigations yielded results summarized in the accompanying charts. Except in the case of balsam they represent averages of several logs. It is regrettable that the work was not restricted to carefully standardized samples, so that completely reliable averages might be compiled. There are, however, compensations in that some estimate can be formed of the variability of the material—a variability that is apt to give rise to quite erroneous conclusions. Thus the density of the birch blocks (a total of 83 blocks cut from 13 logs) varied from 0.51 to 0.71, the greatest range in a single log being from 0.56 to 0.71; the latter density at the centre of the log notwithstanding the fact that the averaged figures from the set of logs indicated a lower density at the centre. Other variations and the vexed question of standardization of samples are discussed in a later paragraph.

Material

With the exception of balsam (a single log cut in October 1928 and left in the field through the winter), the material consisted of four-foot bolts cut in the middle of March 1929 and shipped directly to the laboratory. The logs were used as soon as possible after they were received, but a delay of about two weeks was unavoidable, and the figures quoted for moisture and gas content are subject to correction. The amount of drying taking place in two weeks is not known with certainty, though there are reliable figures for poplar that suggest a more rapid drying in that species than might have been expected (Fig. 11). No corrections, of course, are needed for the determinations of wood, density and swelling.

The discs for sampling were taken one foot from the end, sufficiently far, in all probability, to avoid error due to end drying*.

Balsam (Fig. 2).

(a) Density. This varied irregularly from 0.30 to 0.34, averaging 0.32.

(b) Swelling. 9% in each of the eight blocks cut.

(c) Wood. 18% to 20% of total fresh volume.

(d) Water. Of little interest here, since it is that of a seasoned log.

(e) Gas. Practically the reciprocal of water, since the wood percentage varied so little.

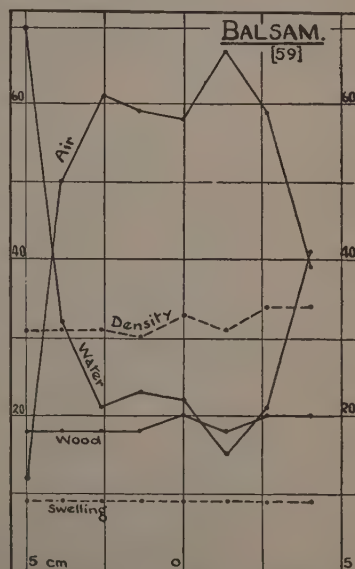


FIG. 2. The distribution of wood, water and gas in balsam.

* This conclusion is based on the result of work to be published later.

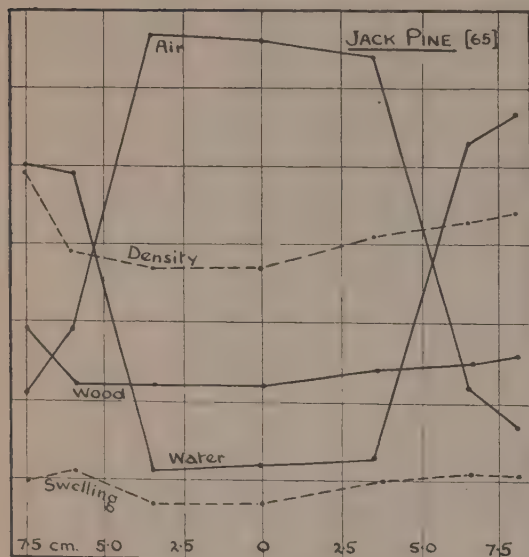


FIG. 3. The distribution of wood, water and gas in jack pine.

stantly low one in the heartwood (Fig. 3). When slender logs are used and a few sample blocks taken, this fact remains unnoticed, and results such as those shown in Fig. 4 are obtained. The figures obtained for density, swelling and wood, of course, are not affected, except in so far as there is any considerable and regular difference between heartwood and sapwood in these features.

(a) Density. In four logs of jack pine the density averaged about 0.39 at the centre and 0.45 at the outside. This is not altogether surprising, as the early wood is formed during rapid growth, the cells being relatively large, with proportionately thinner walls.

(b) Swelling, as might be expected, was also least with wood from the centre of the log, the figures obtained averaging about 8% for that region and 12% for the outer sapwood.

In view of the great irregularity in the water content of balsam, similar lack of uniformity in density and percentage of wood might be anticipated. This is not suggested in this single log, but will be made the subject of further investigation.

Jack pine (Fig. 3 and 4).

The results exemplify in a very clear manner the difficulties caused by lack of uniformity of the samples. The curve for the distribution of water in freshly cut soft wood, with the possible exception of balsam, shows a fairly uniform, very high water content in the sapwood, and a con-

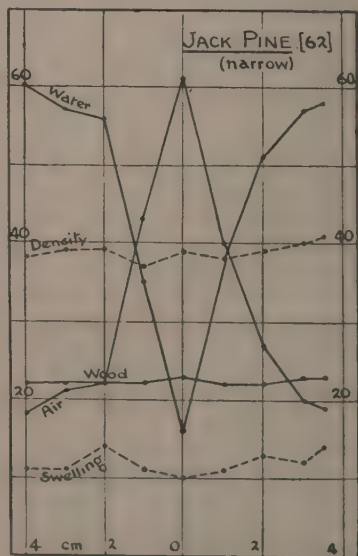


FIG. 4. The distribution of wood, water and gas in jack pine with a narrow heartwood.

(c) Wood was present to the extent of a little over 25% in the sapwood and barely 23% in the heartwood.

(d) Water. The heartwood contained about 12% of water (except in log 62, the very narrow heartwood of which had 16%). About 52% of the volume of the outer sapwood was water.

(e) Gas. The gas content calculated from the above figures was nearly constant at 60% in the heartwood and about 23% in the outermost samples. Thus a log with a wide heartwood has a large proportion of its cells filled with gas, while one with a narrow heartwood such as log 62 (Fig. 4) contains but little gas, and is a bad "floater".

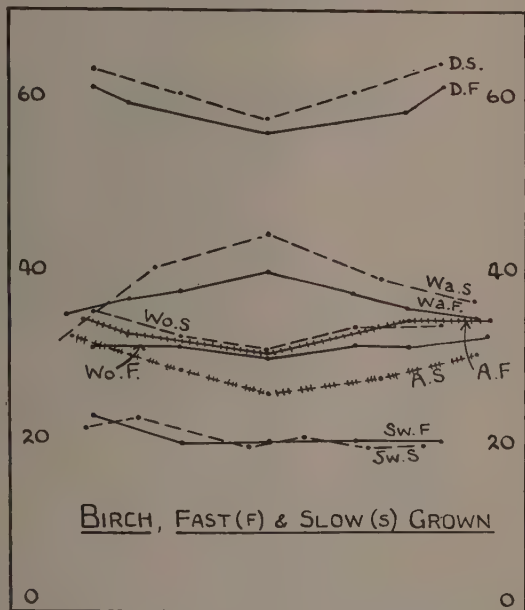


FIG. 5. The distribution of wood, water and gas in slow-grown birch.

Birch (Figs. 5 and 6).

Fourteen logs of very different types were used. The range, which is of considerable importance in a study of floatability, is indicated in Table I.

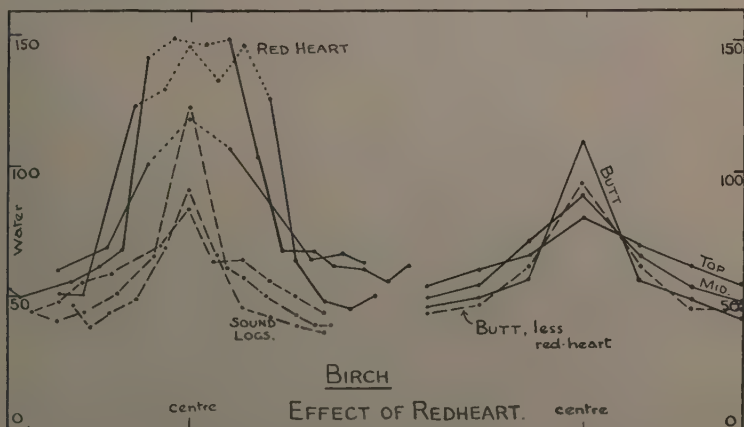


FIG. 6. The distribution of wood, water and gas in birch with red heart.

TABLE I
EXAMINATION OF BIRCH LOGS

Log No.	Section of tree	Rings in last inch of growth	Age of tree at stump, in yr.	Height of sample cut above stump in ft.	Diameter of tree breast-high in in.	Diameter of sample	Growth rate	Remarks
								All cut March 13, 1929
70	Middle	31	131	18	8.5	6.6	Fast	Red heart
71	Top	25	131	38	8.5	4.6	Fast	
72	Top	—	120	18?	6.6	4.4	Slow	
74	Top	—	120	36	10.9	6.4	Fast	
76	Middle	—	120	22	7.3	5.1	—	Red heart
81	Butt	25	59	15	5.4	5.8	Fast	Heart rot
82	Top	23	59	26	5.4	3.9	Fast	
83	Butt	26	60	10	4.1	3.8	Slow	
89	Top	27	59	30	6.4	3.8	Fast	
92	Top	23	52	18	3.8	2.8	Slow	
93	Top	—	120	32	7.7	5.5	Slow	
97	Middle	—	124	13	5.5	4.7	Slow	
98	Top	—	124	30	5.5	3.2	Slow	
99	Top	—	120	50	12.2	3.9	Fast	
201	Top	—	120	38	12.2	5.6	Fast	

The results obtained reflect the heterogeneity of the samples and provide an interesting test for the errors involved by the assumption that the proportion of wood present is constant. The results of Table I indicate two generalizations which, if confirmed, are of importance, although present evidence cannot be accepted as conclusive: (a) Slow-grown logs may contain a higher proportion of wood, and consequently have a higher density, and water content, two factors tending to reduce their floatability (Fig. 5). (b) Red heart, which occurs frequently in birch, particularly in butt logs, may indicate a much higher water content (Fig. 6). Against these generalizations may be opposed the facts that (a) is based on the results obtained on six logs only, and that (b) is not always true. Determinations made in February, 1930, on three sound trees and three with red heart, of different ages, revealed no appreciable difference. It can only be stated that in the present set of logs conditions were as reported.

The following figures will illustrate the results obtained:

(a) Density. The lowest recorded density was 0.51 (once), and the highest 0.71 (thrice), the average being 0.66. Most logs were denser towards the outside (Fig. 5), but some were denser towards the centre. Log 93, for example, gave the following figures: outside, 0.60, 0.63, 0.65, 0.71; centre, 0.71, 0.64, 0.58, 0.56 outside.

(b) Swelling did not follow the density. It varied very considerably, values as high as 31% and as low as 10% being recorded. These possibly are faulty, but 23% and 24% are certainly correct; as low a value as 17% was recorded several times. The average was about 21%.

(c) Wood averaged about 33%, usually highest near the outside. The lowest percentage recorded was 28, the highest 39. As might be expected, the results varied almost directly with density, variations in swelling causing slight deviations.

(d) Water. The logs constantly had a higher water content towards the centre, averaging about 40%, and near the outside about 32%. These figures are not exactly those of freshly cut wood at this season, as practical considerations delayed the analyses for about two weeks. Drying during this time is very considerable in poplar (Fig. 11), but probably less in birch. In any event, these values obtained in March, 1929, differ but little from those obtained in February, 1930. The results, based on dry weight, are plotted in Fig. 9.

(e) Gas. The volume of gas present in the sapwood was about the same volume as that of water, dropping in the centre (as the water rose) to a little under 30%.

Poplar (Fig. 7).

Only four logs of poplar were used. These were cut at the same time as the birch, March, 1929, and were quite varied as shown by the results in Table II.

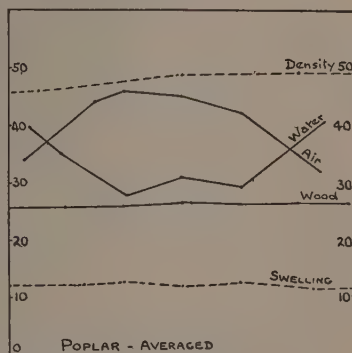


FIG. 7. The distribution of wood, water and gas in poplar.

TABLE II
EXAMINATION OF POPLAR LOGS

No. of log	Section of tree	Annual rings in outside inch of growth, in years	Age of tree at stump	Height of sample cut above stump, in ft.	Diameter of tree breast-high, in inches	Diameter of sample in inches	Rate of growth
205	Top	6	60	12	6.3	4.8	Fast
206	Middle	17	58	16	11.0	7.6	Fast
207	Top	19	58	32	11.0	4.4	Fast
209	Top	11	60	27	9.1	6.0	Fast

The results are summarized in Fig. 7.

(a) Density. The density varied considerably and irregularly, which is rather surprising, for poplar is considered as a singularly uniform wood. It has been found, however, in later work, that the water content also is variable. Log No. 209 showed a decided lack of symmetry in distribution of material, the density values obtained being: Outside, 0.48, 0.45, 0.43, 0.44, centre, 0.58, 0.57, 0.59, outside. The other logs were more uniform but densities ranged from 0.37 to 0.55.

(b) Swelling. The difference between fresh and dry volume was small, averaging only about 12%, and ranging from 10 to 15, with no marked regularity.

(c) Wood. The minimum percentage of wood present was 20 and the maximum 34. In log No. 205, which has extremely wide growth rings, there being six only in the outside inch, the wood occupied only from 20 to 25% of the fresh bulk, while in log No. 207, with 19 growth rings in the outer inch, there was 27 to 30% of wood. The average value was about 27%.

(d) Water. The distribution of water differed very considerably from that in birch. It was somewhat irregular but averaged about 30% over the centre half of the logs and increased to about 40% at the outside.

(e) Gas. The gas content of the samples was about one-third the bulk near the outside, and a little under one-half at the centre.

According to the relationship already given, if the density and swelling, and hence the wood, are constant, it is possible to translate moisture content based on dry weight into that based on wet volume, that is, the actual volume of the living tree. It is also possible to calculate the gas content as $100 - (\text{wood} + \text{water})$.

A survey of the results given above shows that the wood and density values are not constant but that there are considerable variations. These are sufficiently large, in the case of birch, to give an error ranging from +13% to -16% and averaging $\pm 6\%$, when density is taken as 0.60 and the ratio of wet to dry volume as 1:2; giving a conversion factor of 0.5. These errors are scarcely reduced by making allowance for the lower (average) density of blocks from near the centre, using the factor 0.49 instead of 0.5.

In the case of balsam, where only a single log was treated in this way, a factor of 0.29 (density 0.32 and swollen volume 1.19) was indicated. For poplar the factor was 0.41 (density 0.46 and swollen volume 1.12). For jack pine a conversion factor of 0.38 was obtained, the density being averaged at 0.42, and the swollen volume at 1.11. In the latter case the error involved is even larger than in birch, though one or two of the extreme figures are possibly due to errors in reading of volume or weight.

It is apparent that the use of conversion figures involves a very considerable error, and the desirability of using such figures becomes questionable. No doubt, however, it is a distinct advantage to be able to express the composition of a log in terms of wood, gas and water on the basis of the volume of the living tree, and the conversion factor supplies the only easy means of arriving at this.

The only solution of the difficulty is an obvious but tedious determination of such figures for standardized lots of logs, and the restriction of seasonal and other measurements to these lots. Progress has already been made in this direction, and seasonal figures have been obtained recently from just such uniform material.

For each season top, middle and butt logs are sampled from each of three, or more, similar trees. These are taken from one area chosen for the uniformity of its trees and it is hoped in this way to reduce as far as possible the errors due to variation in the samples. Even with these precautions there will be a considerable error, but reference to the results for birch obtained in February, 1930 will indicate that this is much smaller than the seasonal and other differences recorded.

Preliminary Notes on the Seasonal Distribution of Water and Gas in Trees

At the moment no more than a brief account can be given of a number of measurements of water content made at various times during the past year. Late summer and fall, which are, perhaps, the most interesting seasons, are not included in these determinations, but it is hoped that reliable analyses will be made during the coming year.

Reference has been made elsewhere to the methods of sampling and to the drying of poplar in the interval elapsing between cutting and sampling.

Of the five species used, two alone, spruce and jack pine, are typical soft woods in that they have very wet sapwoods and well-marked and uniformly dry heartwoods. Balsam is peculiar in that it has an extremely variable water content, a condition which has been suggested as being due to open pits between the tracheids in parts of the heartwood. The matter requires further investigation. Neither of the two hard woods is typical. It is practically impossible in the case of birch to distinguish heartwood and sapwood, a condition reflected in its water distribution. Poplar in many cases does possess heartwood, and this is markedly drier than the broad sapwood. Tylose formation may play an important rôle here, and, this too, is a matter for further study.

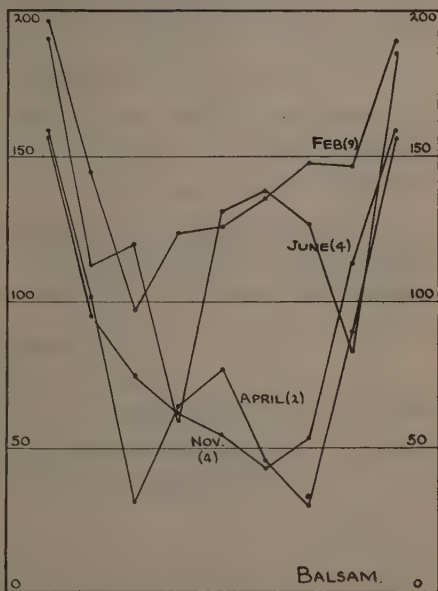


FIG. 8. The seasonal changes of water distribution in balsam.

Balsam (Fig. 8)

The results presented include those for April, June and November, 1929 and February, 1930. Those for February, 1930 alone are derived from a standard lot of top, middle and butt logs from three trees. The others are

from smaller lots, and are therefore less reliable. It is clear that any further work with balsam must make allowance for its tremendous variability, and this will involve the use of larger sample lots and an entirely different method of sampling each log. In the field, it is intended to make analyses of complete discs rather than of strips across the logs, and to correlate the observed variations with factors such as exposure, unequal development of roots and branches, and with the microscopic characters (pit-closure, etc.) of the wood. It is highly probable that this will afford explanation of the variations, at present inexplicable.

Jack Pine

Measurements were made in March, July and November, 1929 and February, 1930. The lots used were as follows:

March: Two top and two middle logs.

There was considerable delay in sampling, and the water content indicated is to be regarded as a minimum rather than as an actual one.

July: Top, middle and butt logs from a single tree.

November: Top, middle and butt logs from one tree and top and butt samples from a second.

February, 1930: A standard lot.

The results are reported in Table III together with those obtained for a single log in August by E. C. Jahn (5). The results are all very similar, and indicate little variation in water content.

TABLE III
WATER CONTENT OF JACK PINE

Date	Sapwood			Heartwood		Remarks
	Outer	Middle	Inner	Outer	Centre	
March	139	—	144	32	37	Delayed analyses, probably low.
July	148	—	132	30	32	Top, middle and butt logs of a single tree.
August	141	124	103	34	32	Ditto, Jahn.
November	160	—	147	33	34	— — —
February	161	—	148	32	33	— — —

Jahn's figures for August are the lowest, as might be expected, the trees having been subjected to at least two months of hot, dry weather when transpiration was rapid. Lower values might well be expected in September and

possibly in October, followed by a rise in late fall and winter. It is to be noted that the heartwood has practically the same water content throughout. This means that relatively large variations in the sapwood would be necessary to affect seriously the total water content of any but top logs. This, naturally, is of considerable practical importance.

Spruce

The analyses recorded are for April, June and November, 1929 and for February, 1930. The last lot alone is standard, the April lot consisting of two tops, that for June of top, middle and butt logs from a single tree, and that for November of middle and top, and butt and top logs from two trees.

The June figures are higher than the others, but since they are from a single tree, the reliability of this indication is questionable. Again the heartwood is uniformly dry with a moisture content of 40%. The outer sapwood contained about 160% of water.

Birch (Fig. 9)

The data are somewhat more complete for this species and the curves are derived from rather larger lots. That marked March 1929, consisted of 14 logs. The results obtained with these appear in Table I. There was delay in sampling but the resulting curve differs but little from those derived from February lots.

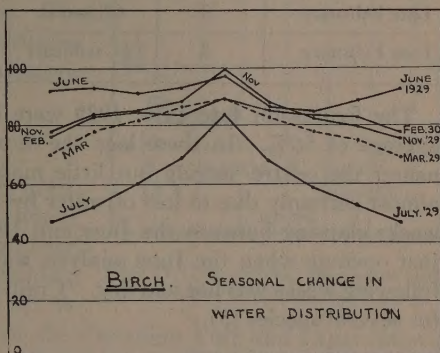


FIG. 9. The seasonal changes in water distribution in birch.

June, 1929: Top and middle and top, middle and butt logs from two trees.

July, 1929: Top, middle and butt logs from each of 10 trees. The trees concerned varied from 6 to 12 in. in diameter but were all of about the same age (60 yr.) as in the standard lots.

November, 1929: Three butts, three middles and two tops from six trees.

February 6, 1930: A standard lot.

February 20, 1930: Same as for February 6, but from three trees of 120 and three trees of 60 yr. The figures derived from this lot are not included in Fig. 9.

Of the six lots recorded that for June gave the highest water content, the average being nearly uniformly across the logs about 93% of the dry weight. The figures for February, March and November were all very similar, but with a rather lower average, about 80%, and with the outer parts of the logs distinctly drier than the inner parts. The very complete figures for February

were due to the sampling of trees for a girdling experiment, and provided an opportunity of comparing standard lots. The average values are given in Table IV to show how nearly they correspond. In this case redheart seems to have had practically no effect, which is somewhat surprising after such positive results were produced in March of the preceding year (Fig. 6).

TABLE IV
AVERAGE WATER CONTENT OF BIRCH LOGS

Date cut	No. of trees	Age, condition	Position of samples								
			Outside			Centre			Outsid		
Early February	3	60	74	85	83	84	92	85	83	82	75
Late February	3	60, sound	79	83	86	93	105	90	83	83	79
Late February	3	120, redheart	82	88	90	92	86	95	92	88	80

The figures for late July, 1929 were by far the lowest recorded, with an average of 56%. In these logs the outer rings were much drier than those nearer the centre, having but little more than half as much water. This is almost certainly due to loss of water by transpiration during the six or seven weeks elapsing between the June and July determinations. The leaves were just opening when the June analysis was made and the weather during the following weeks was hot and dry. Craib (1) obtained somewhat similar results for several species (5).

Poplar (Fig. 10 and 11):

The curves are based on the results obtained from four lots:

March, 1929: One middle and three top logs.

November, 1929: Top, middle and butt logs from two trees. There was an interval of two weeks between cutting and sampling, and this, (Fig. 11) is sufficient for considerable drying.

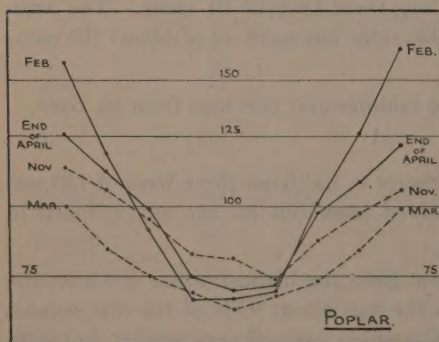


FIG. 10. The seasonal changes in water distribution in poplar.

February, 1930: A standard lot.

April 30, 1930: A standard lot.

Of this material the February and April lots alone are reliable. There is but little difference in water content, except in the outer layers of the samples. The indication of lower water content in the outer rings in April is somewhat surprising unless the water is moving inward to some extent, as may be indicated by the rather higher figure for the inner rings. The figures for this species are too meagre to supply

the basis for any speculation, and must be supplemented before discussion can be profitable.

There are indications of difference in water content between top, middle and butt logs of the trees used, but discussion of this will be reserved until further work has been completed. The possibility of very rapid changes in water content as reported by Hartig (3), must not be overlooked. His results point to a higher water content at night than in the daytime. The lumberman, however, cuts the trees during the day, and Hartig's findings, therefore, lose some of their significance.

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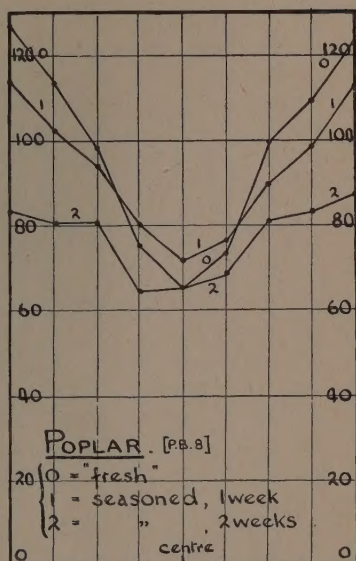


FIG. 11. The seasonal changes in water distribution in poplar.

References

1. CRAIB, W. G. Royal Botanical Gardens, Edinburgh, Scotland 11 (51): 1, 1918; 12 (59): 187, 1920; 14 (66): 1, 1923.
2. GREW, N. The Comparative Anatomy of Trunks, Together with an Account of their Vegetation Grounded Thereupon; in Two Parts. 1675.
3. HARTIG, T. A. Bot. Zeit. 26: 17-13. 1868.
4. HAWLEY, L. F. and WISE, L. E. The Chemistry of Wood. 1926.
5. SCARTH, G. W. and JAHN, E. C. Can. J. Research. 2: 409-424. 1930.

